VOL. XLIV 1923

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TRANSACTIONS

OF THE

American Electrochemical Society

VOLUME XLIV

FORTY-FOURTH GENERAL MEETING

DAYTON, OHIO

SEPTEMBER 27, 28 AND 29, 1923

PUBLISHED BY

The American Electrochemical Society

AT THE OFFICE OF THE SECRETARY

COLUMBIA UNIVERSITY, NEW YORK CITY

1924

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VOLUME XLIV 1923

TRANSACTIONS

OF THE

American Electrochemical Society

PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTY-FOURTH GENERAL MEETING OF THE SOCIETY, HELD AT THE HOTEL MIAMI AND THE ENGINEERS' CLUB, DAYTON, OHIO, SEPTEMBER 27, 28 AND 29, 1923.

The registration at this meeting was 88 members and 102 guests, or a total attendance of 190. Registration of members and guests began at 6.00 P. M. Wednesday, on the main floor of the Hotel Miami.

PROCEEDINGS OF THURSDAY, SEPTEMBER 27, 1923

The first session of the Forty-fourth Meeting of the Society was held in the ball room of the Hotel Miami at 10.30 A. M. After a few introductory remarks, President Hinckley introduced Mr. Charles H. Paul, President of the Engineers' Club of Dayton, who most heartily welcomed the Society members and guests to Dayton and to the Engineers' Club. He mentioned briefly the object of the Club in promoting interest in the engineering profession by the co-operation of its members with the local authorities. The Club has every provision for convenience, comfort and beauty that could be desired in an engineers' club, and is one of the finest clubs of its kind in the country.

The papers presented and discussed during the first session, held at the Miami Hotel, were prepared by the following authors: Kenneth M. Watson and O. P. Watts; M. A. Hunter and A.

Jones; George S. Tilley and Oliver C. Ralston; E. J. Casselman; H. C. P. Weber; D. E. Howes. These papers, with discussions, are printed in these Transactions.

At 12.30 the meeting adjourned to the Engineers' Club, where the program was continued by informal discussions, at luncheon, of the following subjects:

I. Electric Furnace Brass Foundry Practice (H. W. Gillett, Presiding)
II. Electrodeposition (Walter Fraine, Presiding)
III. Organic Electrochemistry (C. J. Thatcher, Presiding)
IV. Utilization of Chlorine (A. H. Hooker, Presiding)

These Round Table Discussions proved to be a successful and interesting innovation, and by three o'clock, the time scheduled to leave for McCook Field, animated discussions were still under way, the electric brass group continuing its session until five o'clock. A brief summary of the points brought up at the "Round Tables" is given below.

I. The Round Table on Electric Furnace Brass Foundry Practice, Dr. H. W. Gillett, chairman, was attended by about 90 members and guests, representing central stations, electric brass furnace manufacturers, rolling mills, electric equipment, and electrode companies. Approximately half of those in attendance were either users of electric brass furnaces or were contemplating their installation.

Electric furnace users agreed unanimously that, although the quality of the metal obtained in electric melting was no better than that obtained from properly operated fuel-fired furnaces, the metal was more uniform and the losses lower than with fuel-fired furnaces. The quest for better refractories continues; the high initial cost of an electric furnace and the higher cost of power when little is used, or when furnaces are operated intermittently during periods of depression, are factors that discourage the small user. Notwithstanding these drawbacks, brass manufacturers have found that over-all melting costs are less with electric than with fuel-fired furnaces.

The demand for better refractories is urgent; that is, for refractories that will permit the operation of induction furnaces

on alloys of over 75 per cent copper without the necessity of a shut down for relining at too frequent intervals. The rammed-in and the pre-formed linings give poor results. The users stated that if the life of a reliable lining for high copper alloys were even as short as a fifth of the average life for yellow brass, it would pay to use the induction furnace.

Improvement in refractories seems to be the key to the extension of induction furnace melting and to be of vital importance in the use of the other types. This subject of refractories will comprise part of the technical program of the next two meetings of the Society.

II. Mr. Walter Faine, of the National Cash Register Co., was chairman of the Electrodeposition Round Table. Subjects such as the co-operation with government laboratories, corrosion resistant coatings, stripping of plated metals, filtration of large volumes of electrolyte, and plating aluminum and aluminum alloys were brought up in the discussion.

III. At the Round Table on Utilization of Chlorine, at which Mr. A. H. Hooker of the Hooker Electrochemical Co., presided, there were present representatives from various chlorine producing companies, besides others interested in its uses. It was pointed out that since chlorine had always been a product of direct manufacture in this country, uses should be sought which could bear the entire burden of cost for commercial production. Among the suggested uses for chlorine which would permit of its production on a continuous, economical and increasing scale were:

1. The production of zinc chloride for timber preservation and fire-proofing, a use that could be largely extended to the benefit of the country in conserving timber. The chief obstacle to the manufacture of zinc chloride is the lack of a sufficient supply of scrap zinc.

2. The production of a pure grade ammonium chloride particularly adapted to the growing needs of the dry cell industry. Large quantities of the denser grade are also used for metal cleaning and soldering. The quantity required to meet present day needs was estimated at approximately 25,000 tons per annum. At present a sufficient quantity of the pure grade cannot be obtained.

3. The production and use of aluminum chloride for oil cracking and particularly for the manufacture of anthraquinone, a dye base used for the production of fast vat dyes.

4. The possibility of using chlorine in place of sulfuric acid, viz., chlorination instead of sulfurization in breaking down organic compounds and in forming organic dyes and derivatives.

5. The treatment of clear sewage effluent with chlorine. With the growing pressure exerted by state boards of health, the use of chlorine for this purpose of protecting public health will be materially extended.

6. The uses of sodium hypochlorite, and its value for general household and farm use, were discussed with a great deal of interest. It was suggested that the Department of Agriculture might find it advantageous to prepare a special bulletin on this subject.

7. In garbage incinerators and sulfate pulp mills small quantities of chlorine are used as a deodorizer.

8. A large future field for the use of hypochlorite, though by no means a new one, is in the sweetening of petroleum oils, removing sulfur compounds and in reducing the sludge losses from sulfuric acid.

IV. Dr. C. J. Thatcher was chairman of the Round Table Discussion on Organic Electrochemistry, at which the present status of this art was reviewed, particularly with reference to the organic compounds that are now being made commercially. Inquiries of various synthetic organic chemical manufacturers indicated that only a limited number of them are now conducting research along this line; the commercial developments are few in number. Paraphenylenediamine is a product which has been made on a quite large scale by electrochemical means. A product that is rapidly approaching commercial manufacture is benzidine, which is electrolytically produced from nitrobenzol.

The visit to the Air Service Engineering Division of McCook Field, Thursday afternoon, gave the members and guests of the Society an excellent idea of the investigations which are continually being made for the purpose of improving and perfecting

aircraft. The following sections were visited: chemical laboratories, camouflage, fabric testing, wood testing, metallurgical laboratory, wings and fuselage unit, pattern and model unit, machine shop, metal shop, power plant laboratory and hangars.

At about 5 o'clock the trip was continued to the Miami Conservancy, where the Englewood Dam on the Stillwater River was inspected. In all there are five such dams above Dayton, which serve to protect Dayton and the towns farther south against any destruction by a flood. The automobiles, which were kindly provided by members of the local committee, then brought the parties to Triangle Park, where a dinner and smoker lent enjoyment to every one. President Hinckley acted as toastmaster, and the entertainment which followed included music, talks by F. A. Lidbury on the "Electrochemistry of Golf," and E. F. Northrup on the "Electrochemistry of Dogs." The main feature of the evening, however, was the address by Mr. Chas. F. Kettering, President of the General Motors Research Corp. His long experience as a research engineer made his address both inspiring and interesting. A few of his sparkling remarks are quoted below:

"The technical staff of any industry will accept anything new if it is just like what they had before, and research sometimes makes a great mistake by tying the package up in red paper instead of brown paper, when the industry has always been used to getting it in brown paper.

"What we need today is a correlation among the so-called sciences.

"Our engineering research today lacks the question of fundamentals. We tackle problems superficially. When we finally solve them by the simplest type of thing, everybody recognizes that it is the only thing that would have worked in the first place, but it would not have been research without our trying everything on earth but the right thing. The only time you do not want to fail in a research problem is the last time you try.

"Research is a perfectly definite thing and research problems are gotten in a perfectly definite way . . . . There are a thousand and one problems about the thing that you are doing today which need attention, and perhaps the most standardized things in your

industries are the ones to pick out first, because standards are likely to be mistakes which keep your industry from progressing. When an organization standardizes a thing, and it is found to have been standardized for ten years, that is a good clue for investigation. The only problem in attacking such a research as that is the problem of psychology, and it is 20 per cent scientific research and 80 per cent psychology.

"The facts in any industry are not hidden at all, but we do not see them for reason of a pair of glasses that we wear called 'experience.' If there is any thing in the world that blinds most people to the future development, it is their past experience. They tried something out once and it did not work, so they are never going to try it out again as long as they live.

"The law of accident is responsible for a great many important things accomplished in research laboratories, which I have analyzed as follows: the Lord gets so tired of watching you that He pushes you into the solution of your problem. You then describe your product as the result of a scientific investigation.

"Have all the theories you want, but do not keep them too long, because the facts remain as they are, entirely independent of your theories.

"I have mentioned these various things because we go through life with a lot of impressions about certain things, and they determine whether or not we actively approach a problem or whether we passively die."

At the conclusion of Mr. Kettering's address, President Hinckley expressed the Society's appreciation for this splendid message. The program of the evening was concluded with motion pictures showing various activities at McCook Field.

PROCEEDINGS OF FRIDAY, SEPTEMBER 28, 1923

The Society convened at 9.30 A. M. at the Engineers' Club. President Hinckley introduced Dr. Duncan MacRae, who was primarily responsible for having secured the excellent papers for the symposium on "Electrochemistry of Gaseous Conduction." Dr. MacRae assumed the Chair, and in opening the symposium called attention to the fact that some of the papers on the program constituted a series of reviews and summaries on that part of the

subject which has been practically entirely neglected in textbooks on electrochemistry.

The symposium was appropriately opened by the presentation of a paper on "Electrochemistry of Gases" by Dr. S. C. Lind. This was followed by the reading and discussion of papers by the following authors: F. H. Newman; Research Staff, G. E. Co., Ltd., London, C. C. Paterson, Director; Saul Dushman; K. T. Compton; H. A. Wilson; A. E. R. Westman and W. J. Clapson; and Preston R. Bassett. These papers, together with the discussions, are printed in this volume.

At 2.30 P. M. the Symposium was continued by the presentation and discussion of papers by the following authors: D. McFarlan Moore; Karl B. McEachron; F. O. Anderegg; A. Guenther-Schulze; Frank E. Hartman; Farrington Daniels, Paul Keene and P. D. V. Manning; A. Keith Brewer and Farrington Daniels; and L. Hamburger. All these papers, with discussions, are printed in these Transactions.

A fitting conclusion to the day's symposium was an illustrated experimental lecture by Dr. H. B. Wahlin, of the University of Wisconsin, on "Recent Researches on the Electrochemistry of Gaseous Conduction." This lecture and the demonstration of the Sperry searchlight took place at the Engineers' Club, and were received with great enthusiasm.

Some of the members visited industrial plants during the afternoon. Among these plants were: American Rolling Mill Co., Delco and Delco Light Companies, Duriron Co., General Motors Research Corp. and the National Cash Register Co. These trips were of exceptional interest to members of the Society, and it was largely through the efforts and efficient guidance of Messrs. H. M. Williams and E. H. Kramer of the General Motors Research Corp., that these opportunities were made available.

The Miami Valley Country Club was the scene of a golf tournament in which Messrs. T. F. Baily and R. W. Milnes exhibited unusual skill, which won each a silver trophy.

The ladies were the guests of the Duriron Co., on Thursday, at the Polo Hunt Club; and on Friday Mrs. Edith McClure Pat-

terson entertained them royally at the plant of the National Cash Register Co.

PROCEEDINGS OF SATURDAY, SEPTEMBER 29, 1923

On Saturday morning at 9.30 A. M. the session for the reading and discussion of various papers on Electrodeposition and Electroplating was called to order by President Hinckley. Papers were presented by the following: A. Harold Heatley; W. Blum and H. S. Rawdon; A. Kenneth Graham; M. Knobel and D. B. Joy; Kevie W. Schwartz; S. Field and W. E. Harris; and Louis Kahlenberg and John Vernon Steinle. In addition to these papers and discussions, there are included in this volume four papers, with discussions, which had been presented at the Forty-third Meeting of the Society, by the following authors: W. Blum and H. S. Rawdon; H. E. Haring and W. Blum; A. Kenneth Graham; and M. R. Thompson. These four papers cover pages 305-396 of this volume.

In concluding the Forty-fourth Meeting, President Hinckley, on behalf of the Society, thanked the members for their active co-operation and participation in the discussions, and called upon Dr. Hering to present the

RESOLUTION OF THANKS.

WHEREAS, The success of the Dayton Meeting has been due so largely to the hearty co-operation of local organizations and individuals, it is

Resolved, That the American Electrochemical Society extend a vote of appreciation and thanks to the following:

American Rolling Mill Co.
Delco
Delco Light Co.
Duriron Co.
General Motors Research Corp.
National Cash Register Co.

for opening their plants to us.

To Dr. H. B. Wahlin, of the University of Wisconsin, for his interesting illustrated lecture on "Recent Researches on the Electrochemistry of Gaseous Conduction."

To Mr. Chas. F. Kettering, of the General Motors Research Corp., for his inspiring address.

To the Engineering Division of the Air Service of McCook Field for their hospitality at the McCook Field, and for making it possible to demonstrate the Sperry high intensity arc light at our meeting hall.

To the members of the staff of the General Motors Research Corp. in supplying the demonstration apparatus for Dr. Wahlin's lecture.

To the Engineers' Club, the local Chamber of Commerce, and the Hotel Miami.

And last, but not least, to the very efficient Local Committee, under the chairmanship of Mr. H. M. Williams, of the General Motors Research Corp.

The meeting adjourned at 1.30 P. M.

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S. V. Cook, Dayton, Ohio
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R. F. Dunbrook, Springfield, Ohio
C. G. Eichelberger, Cincinnati, Ohio
Mrs. G. K. Elliott, Cincinnati, Ohio
Russell Elliott, Dayton, Ohio
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Mrs. C. G. Fink, Yonkers, N. Y.
H. V. Fitzgerald, Erie, Pa.
J. T. Fitzsimmons, Dayton, Ohio
T. E. Foulke, Belleville, N. J.
Harold E. Fox, Pittsburgh, Pa.
Paul W. Gaebelein, Detroit, Mich.
Miss E. L. Gibbs, Bath, England
R. J. Giblin, Flint, Mich.
Henry Gieseke, Elizabeth, N. J.
C. E. Gifford, Middletown, Ohio
L. G. Glesmann, Rome, N. Y.
F. H. Gordon, Sherrill, N. Y.
N. T. Gordon, Newark, N. J.
B. S. Guitteau, Dayton, Ohio

Mrs. Jos. Haas, Muncie, Ind.
H. C. Harrison, Columbus, Ohio
F. E. Hartman, Scottdale, Pa.
J. H. Hunt, Dayton, Ohio
E. Huseman, Cincinnati, Ohio
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C. S. Judd, Kenosha, Wis.
Enoch Karrer, Cleveland, Ohio
F. C. Kelley, Schenectady, N. Y.
Richard K. Kennedy, Dayton, Ohio
R. L. Kenyon, Middletown, Ohio
D. H. Killefer, New York, N. Y.
Sidney Kirkpatrick, New York City
W. S. Kopf, Dayton, Ohio
A. Kunz, Middletown, Ohio
H. O. Leslie, Dayton, Ohio
Frank M. Levy, Huron, Mich.
J. E. Linabury, Detroit, Mich.
K. C. Long, Dayton, Ohio
Leon McCulloch, E. Pittsburgh, Pa.
W. J. McDonald, Chicago, Ill.
K. B. McEachron, Pittsfield, Mass.
H. A. McIlvaine, Cleveland, Ohio
Stuart McLean, Cleveland, Ohio
E. Mack, Columbus, Ohio
D. E. MacLeon, Pittsburgh, Pa.
Thos. Midgley, Jr., Dayton, Ohio
A. L. Morner, Middletown, Ohio
B. C. Morris, Dayton, Ohio
J. C. Mullinnex, Cleveland, Ohio
J. H. Nead, Middletown, Ohio
F. E. O'Neil, Niagara Falls, N. Y.
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H. K. Richardson, Bloomfield, N. J.
C. H. Roemer, Dayton, Ohio
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W. D. Seeley, Syracuse, N. Y.
O. E. Servis, Middletown, N. Y.
G. R. Shaw, Cleveland, Ohio
Clarence Smith, Dayton, Ohio
H. B. Swan, Detroit, Mich.
A. V. Taylor, Middletown, Ohio
J. B. Vernor, Middletown, Ohio
H. B. Wahlin, Madison, Wis.
R. S. B. Wallace, Dayton, Ohio
H. H. Walther, Dayton, Ohio
R. F. Whisler, Dayton, Ohio
Frank C. Whitmore, Evanston, Ill.
A. U. Widman, Detroit, Mich.
O. G. Willey, Bridgeport, Conn.
Mrs. H. M. Williams, Dayton, Ohio
D. V. Williamson, Detroit, Mich.
A. C. Zimmerman, Dayton, Ohio

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

A STUDY OF WATER-LINE CORROSION.[1]

By Kenneth M. Watson[2] and O. P. Watts[3].

Abstract.

Experiments were carried out to determine the cause of water-line corrosion. Strips of zinc, copper and brass were partially submerged into various corrosive liquors. Results indicate that although the depolarizing effect of oxygen is necessary for the corrosion of many metals in certain solutions, the contact of air with the upper surface of a liquid is never directly responsible for the occurrence of water-line corrosion. This phenomenon is caused by the slow downward flow of the heavier film of corrosion products along the surface of the metal, which draws in at the upper surface of the liquid a supply of fresh solution. Since all the metal except that at the surface of the liquid is in contact with partly exhausted solution, corrosion is most rapid at the surface. Although there is an even greater circulation of solution down the face of anodes used in the plating and refining of metals, water-line corrosion does not take place. In that work the rate of corrosion is determined by the distribution of current over the anode surface, which depends on Ohm's law and is only slightly affected (at the usual current densities) by the amount of corrosion product contained in the film of solution that touches the anode.

INTRODUCTION.

The subject of water-line corrosion is one which has been of current interest to scientific investigators of corrosion problems for several years and has gained considerable attention from commercial sources, due to its destruction of valuable apparatus

[1] Manuscript received June 11, 1923.
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and materials in industry. Various theories have been advanced as to the causes of this phenomenon, but little actual experimental research is recorded as having been carried out in an attempt to gain definite information as to the causes and mechanism of the action. The work subsequently described in this paper was undertaken with the view in mind of testing the theories which are current among corrosion specialists and, if possible, of gathering additional information on the subject, which might be of value in understanding and combating the resulting effects.

It might be well at this point to explain what is understood by the term "water-line corrosion." As the name would indicate the expression refers in general to the severe, localized corrosion which is met with in the case of metals which are partially submerged in a slowly corrosive solution. This corrosion takes place over a narrow range at the point where the metal emerges from the liquid, that is, where air, metal, and liquid are all in contact. The corrosion may take the form either of deep pitting, giving a result that resembles the work of a drill press, or of a clean cutting of the metal along a line, almost as though a saw had been used.

One of the first cases of water-line corrosion which was called to the attention of the authors was that of the zinc electrode of an old sal ammoniac cell. The cell had been standing for some time without use, and on taking it apart it was noted that the zinc electrode, although for the most part in fairly good condition, was cut almost in two at a point corresponding to the water-line of the solution. Other cases of severe water-line corrosion have been met in the condenser tubes of sea going ships, where a serious commercial problem results. Further trouble of a more or less serious nature is constantly being encountered in laboratories and manufacturing concerns in the use of metal apparatus in corrosive solutions. A case recently brought up dealt with the failure of a common, galvanized hot water tank, such as is used in nearly every home, by deep pitting and general corrosion at the water-line. Thus it is seen that the subject is one of practical importance, which merits careful attention in the study of the subject of corrosion in general.

One of the explanations of this effect, which has long been held as plausible, is based on the accelerating action which oxygen

has on any form of corrosion. It is argued that, since oxygen can be absorbed from the air only at the surface of the liquid, it would be natural to expect that the concentration of oxygen dissolved would be higher at the surface and therefore corrosion would proceed most rapidly at that point. The fact is further pointed out that in most solutions there is a "creep" of the liquid up the sides of objects partially submerged in them. This would result in a thin film of solution over the metal, which would be in constant contact with the air and therefore probably almost saturated with oxygen which, through its depolarizing action, would greatly accelerate corrosion at that point.

The effect of oxygen on the rate of corrosion is undeniable, and it is probable that the depolarizing effect of absorbed air has considerable to do with water-line corrosion as claimed in the above theory, especially in solutions where there is a marked tendency to "creep." However, careful studies of water-line effects produced in the laboratory have caused at least one author to disagree with this theory. In the fifth report to the Corrosion Committee of the Institute of Metals,[4] by Guy D. Bengough, R. M. Jones, and Ruth Pirret, the following statement is made:

"It is a familiar fact that an increased amount of corrosive action is liable to occur in the neighborhood of an air, sea-water surface in contact with certain metals and alloys as compared with that of the immersed portions of the same materials. It is usually supposed that such increased action occurs at or just below the waterline, and that it is due to the depolarizing action of the air whereby electrolytic action is greatly stimulated. A little investigation however soon shows that it is by no means as simple as would be expected on this view . . . . . It soon became clear that the greater part of the increased corrosive action did not usually occur at the water-line but above it and sometimes considerably above it, *e. g.*, as much as 2 cm. . . . . The "water-line" attack in neutral liquids may be considered as essentially a deposit type of attack and is set up because the conditions near the water line are favorable to the formation of harmful deposits from the products of corrosion; and the whole action is no doubt assisted by the oxidizing action of the air."

[4] Journal of the Institute of Metals, 23, 125.

In a further discussion[5] on the protection of condenser tubes, Mr. Bengough states that, "As an instance of attack by corrosion products the well known effect of preferential attack at a water line is an example. This is mainly dependent on the nature and distribution of the products of corrosion and is *not,* as is usually supposed, due principally to the depolarizing action of the air. Under certain conditions the products of corrosion may give rise to "concentration cells," which may give rise to very rapid pitting."

Because of the importance of the problem and the interest shown in it the following experimental work was undertaken in an attempt to straighten out the diversified theories which prevail at present, and to gather additional information on the mechanism and effects of water-line corrosion.

RECORD OF EXPERIMENTAL WORK.

The metal specimens used in the following experiments were for the most part cut from sheets of about 0.37 mm. thickness, the usual size being about 2.5 x 15 cm. These specimens were bent at right angles at a point about 3.75 cm. from one end and set in the solution in which they were to be tested, contained in ordinary tumblers. The bent-over end of each rested against the inner wall of the tumbler just below the top and served to keep the specimen in an upright position and away from the sides. The tumblers were filled with the solutions to within about 1.2 cm. of the top and in some cases connected to a Mariotte bottle to maintain constant levels. In the majority of the cases, however, the water which was lost from the solution was replaced by daily additions. The slight variation of water-line did not appreciably affect the results as compared with those obtained when using the constant-level device.

In preliminary experiments it was found that when corrosion is accompanied by vigorous evolution of gas, as in the attack of zinc by dilute hydrochloric acid, water-line corrosion does not occur. The choice of corroding solutions was therefore limited to such as did not cause liberation of gas.

Samples of zinc were exposed in dilute hydrochloric acid and in solutions containing about 100 g. per L. of sodium chloride, po-

[5] Journal of the Institute of Metals, 26, 442.

tassium nitrate, and ammonium nitrate, and also in a nearly saturated solution of calcium chloride. In the hydrochloric acid, as stated above, there was no evidence of water-line corrosion. There was no water-line corrosion in ammonium nitrate in 20 days, but under the layer of salt which covered the zinc for a distance of 2.5 cm. above the surface of the liquid the zinc was deeply pitted, and at the upper edge of this deposit the zinc was cut nearly in two. In the other solutions corrosion was so extremely slow that there was no noticeable effect at the end of the period of 3 months, to which the experiments were limited.

After 8 days in normal hydrochloric acid sheet copper was corroded entirely in two at a point 1 mm. below the water-line. Brass behaved similarly in a slightly longer time. In normal sulfuric acid corrosion of copper and brass was much slower than in hydrochloric acid, and, strange to relate, the maximum corrosion occurred 3 to 5 mm. *above* the water-line, beneath crystals of metallic salts which had formed there through "creeping" of the solution. In 40 days holes were eaten entirely through the metal at that point. Exclusion of air by a layer of lubricating oil entirely stopped corrosion. In dilute hydrobromic acid water-line corrosion was well-marked on copper in 10 days. In solutions of chromic, formic, acetic, phosphoric, fluoboric and fluosilicic acids corrosion was so slow that no results were obtained in the time available.

A narrow band of cheese cloth was tied tightly about the middle of sheets of brass and copper, and these were then placed in hydrochloric acid so that the cloth extended both above and below the water-line. In 9 days specimens were cut entirely in two at both edges of the cloth, and also showed deep cuts at the water-lines, as well as general corrosion over the whole surfaces. When air was excluded by pouring on a film of oil, corrosion below and at the water-line was stopped, but the sheet was severely corroded in the air at the top of the cloth. That air (or oxygen) is necessary for the corrosion of brass and copper in hydrochloric and sulfuric acids is amply confirmed by these experiments.

Sheets of copper were fastened to the bottoms of tumblers which were filled with hydrochloric acid, inverted in larger dishes of the same liquid, and supported above the bottom so that half of the

tumbler was above the acid in the outer dish. Hydrogen was then passed into the tumbler until the liquid level was the same within as without the tumbler. Any air that reaches the copper must come in from below, and if water-line corrosion is due to a higher concentration of depolarizing air at the upper surface than throughout the main body of liquids, the most rapid corrosion in this case must take place at the bottom of the sheet of metal. At the end of 15 days the specimen was completely cut off at the water-line. This establishes definitely that even where oxygen is necessary in order that any corrosion may take place, water-line corrosion is not due to any particular depolarizing action at the boundary surface between air and liquid.

Several experiments were tried in which the corrosion of copper in hydrochloric acid was stimulated by addition of an oxidizing agent to the liquid, instead of waiting for oxygen to be absorbed from the atmosphere. Both bromine and potassium dichromate were used as oxidizing agents, with the vessels open to the air, and also covered with a layer of oil. There was sharp water-line corrosion in every case, and access or exclusion of air seemed to be without effect.

The true explanation of water-line corrosion was suggested by a phenomenon frequently seen during the corrosion of metallic anodes by use of the electric current, where the dissolving of the metal creates a film of denser solution next to the metal, which can be seen to flow down along the surface of the anode and stream off from its lower end. Water-line corrosion was thought to be due to a similar circulation which keeps all of the metal plate except that near the liquid surface in contact with partially exhausted solution, and causes the metal at the surface of the liquid to be bathed by the stream of fresh solution which is drawn in to take the place of that which flows downward along the metal surface.

To determine if such circulation actually takes place in cases of water-line corrosion a strip of copper was placed in a narrow stereopticon cell containing normal sulfuric acid, to which 50 g. per L. potassium dichromate had been added, and the progress of

corrosion watched by transmitted light. In a few minutes the expected circulation was clearly visible, and a constant stream of corrosion products flowed down the specimen and off from its lower end. A slight flow across the surface of the solution to the copper was also detected. Similar examination of a strip of copper in dilute nitric acid showed quite different results. In this case there was a slight current flowing toward the metal at the bottom and then upward along the metal surface. This was caused by a slow evolution of gas at the surface of the metal, which acted like an air-lift pump and prevented the downward flow that would otherwise have taken place. Experiments not previously mentioned had shown that water-line corrosion of copper in dilute nitric acid does not occur, but while corrosion is fairly uniform, it is slightly greater at the bottom than elsewhere. The reason for the failure to secure water-line corrosion of zinc in hydrochloric acid, mentioned earlier, is apparent.

The above view of the nature of water-line corrosion is confirmed by the following experiments: A narrow strip of copper was suspended in a solution of hydrochloric acid containing potassium dichromate, and an open glass tube was placed around it so that the tube dipped 2.55 cm. into the solution. In 2 days the copper was cut through, not at the liquid surface, but opposite the bottom of the tube. The same result was obtained in a longer time in hydrochloric acid, without the addition of any oxidizing agent but exposed to the air.

A sheet of copper was suspended in a tumbler so that half of it was above and half below a perforated paraffin disc, which extended horizontally across the tumbler, and the tumbler was filled with normal hydrochloric acid. In 8 days the regular water-line corrosion had taken place, and the specimen was cut through at the surface of the solution. On removing the remainder of the specimen from the solution it was found that corrosion had been almost as severe immediately below the paraffin disc as at the surface of the liquid, and the metal was nearly cut off at that point.

When a strip of copper was suspended in hydrochloric acid containing potassium dichromate and circulation was caused arti-

ficially by a small, electrically-driven propeller, the specimen was cut off in 2 days, but opposite the propeller instead of at the water-line. In plain hydrochloric acid exposed to the air the same result was obtained.

DISCUSSION.*

COLIN G. FINK[1]: I do not altogether agree with the authors in their general theory. It has been our experience that the air is a great factor in the corrosion of anodes. In the development of insoluble anodes for various electrolytes, we have repeatedly observed that alloys which are very resistant to the electrolyte if completely submerged in the electrolyte may, if partially exposed to the air, corrode rapidly at the solution line.

ALEX LOWY[2]: Has any work been done in regard to nitrogen or other gaseous layers? I think an experiment of this type would either eliminate the oxygen theory or else be ideal for that particular explanation.

C. J. RODMAN[3]: Possibly I can answer that question. With an oxygen or air atmosphere above the liquid, the terminal at the liquid gas junction corroded noticeably. We wanted to find some way of getting away from that type of corrosion, and tried inert atmospheres. This cut down corrosion substantially. By coating the metal at the liquid gas junction with inert materials, such as waxes or glass, the corrosion was obviated entirely. It has been suggested that oil be used to float over the aqueous solution to effect a non-corrosion of the metal at the liquid-gas junction. This procedure does lessen corrosion but, due to about 12 to 15 per cent by volume solubility of O_2 in oil, corrosion is still possible, yet the conditions of the experiment admit of a liquid junction of electrolyte and oil which does away with the high surface tension and concentration effects.

If the authors had been a little more comprehensive in their title

* In the absence of the authors the above paper was presented by Colin G. Fink.

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[2] Professor of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

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and discussed types of liquid line corrosion, other phenomena, such as oil-air junction corrosion could be discussed to advantage here.

Beautiful examples of this occur in oil insulated apparatus, and would possibly lend valuable data in explaining some of the interesting phenomena on water line corrosion.

COLIN G. FINK: Referring to the authors' tests in an atmosphere of hydrogen, there is one point that we forgot and that is the spray effect, which is also very important and has a lot to do with this air line corrosion. Oxygen gas at the anode takes with it a certain amount of electrolyte. There is a constant wash of electrolyte plus air over the electrode surface right above the solution line. If you can eliminate the spray, *e. g.*, by covering the electrolyte with a film of oil, in a large number of cases your "necking" disappears. That oil test is similar to the test of using an inert atmosphere. If you exclude the air, most "necking" disappears.

W. B. SCHULTE[4]: One of the troubles that arise in the discharge of dry cells is the cutting off of the zinc can at the top point of the electrolyte, whether the electrolyte is held in a blotting paper, or whether it is in what is known as a paste electrolyte. The cutting through of the zinc at the surface is something that we try to avoid.

EDWARD C. SMITH[5]: I think we have always experienced that same difficulty, but have found no particular remedy for it. When we have tried covering any area of active zinc, we have, of course, increased the current density beyond it, which resulted in the metal being eaten through to a greater extent close to the area blocked off.

LEON MCCULLOCH[6]: May I call attention to a chemical reaction that may take place at the water line surface, such as you may have in dry cells exposed to ammonium or sodium chlorides.

Suppose we have a strip of zinc partially submerged in a solution of sodium chloride and above it air or oxygen. The

[4] C. F. Burgess Labs., Madison, Wis.
[5] National Carbon Co., Inc., Fremont, Ohio.
[6] Research Dept., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

oxygen will depolarize hydrogen and give you a flow of current across the water line surface. Above you will have NaOH formed and down below you will have zinc chloride formed. That gives an alkaline area above and a neutral area below. The alkali possibly attacks the zinc, liberates hydrogen, and results in a chemical reaction right at the surface.

KENNETH M. WATSON (*Communicated*): In reply to Dr. Fink's discussion I wish to say that it was not intended in this paper to make any statement to the effect that oxygen is not necessary for corrosion in general, or that it has no influence on water line corrosion. In many cases corrosion cannot proceed at all without the presence of oxygen in some form, and action in all ordinary cases is probably accelerated by the addition of oxygen. The point made was that in certain cases in which corrosion is able to proceed independent of the oxygen of the air, as when an oxidizing agent exists in the solution, the water line effect will be obtained even though there is no contact of the liquid with the air. This fact disproves the theory that water line corrosion of that type is due to a higher concentration of oxygen dissolved from the air at the surface.

It is difficult to conceive of the application of the circulation theory of water line corrosion to the cutting off of the zinc cans of dry cells. This type of corrosion is evidently different from any of those studied, and it is possible that Mr. McCulloch's explanation is the correct one.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

THE REDUCTION OF SOME RARER METAL CHLORIDES BY SODIUM.[1]

By M. A. Hunter[2] and A. Jones[2].

Abstract.

The success which had attended the production of metallic titanium[3] led to the belief that other metals might be prepared in coherent form by the reduction of their anhydrous chlorides by sodium. The method has been tried out with the chlorides of beryllium, chromium, uranium, vanadium and zirconium with varying degrees of success. The main difficulty lies, not in the reduction itself, but in securing enough of the anhydrous chlorides to reduce. If sufficient quantities of the chlorides were available we do not doubt that all of the metals mentioned could be obtained in metallic form. With the limited quantities of the chlorides which have been prepared on a laboratory scale we have succeeded in obtaining beryllium, chromium and zirconium in a more or less granular form, but with uranium and vanadium, metallic powders only with varying degrees of purity have been produced. Further details for each metal are given under the headings of the separate metals.

THE REDUCTION BOMB.

Three types of reduction bombs have been made during the progress of the work. A small bomb was first constructed for preliminary investigations, where small quantities only of material were available for reduction. This was made from a solid steel cylinder 12.7 cm. (5 in.) deep and 7.6 cm. (3 in.) in diame-

[1] Manuscript received March 28, 1923.

[2] Rensselaer Polytechnic Institute and Driver-Harris Co.

[3] J. Am. Chem. Soc. 32, 330 (1910); Orig. Comm., Eighth Int. Congress, App. Chem. 2, 125.

ter. In this forging a hole 3.8 cm. (1.5 in.) in diameter was bored. The cylinder was provided with a flange 10 cm. (4 in.) in diameter and a lid 5 cm. (2 in.) deep which fitted on the cavity in the cylinder. The bomb was maintained airtight by an intervening gasket of soft copper which was pressed into grooves in the bearing surfaces of the cylinder and the lid. The lid was held in position by a steel yoke fitting over the flanges and pressing on the lid by means of a single threaded 1.9 cm. (0.75 in.) bolt.

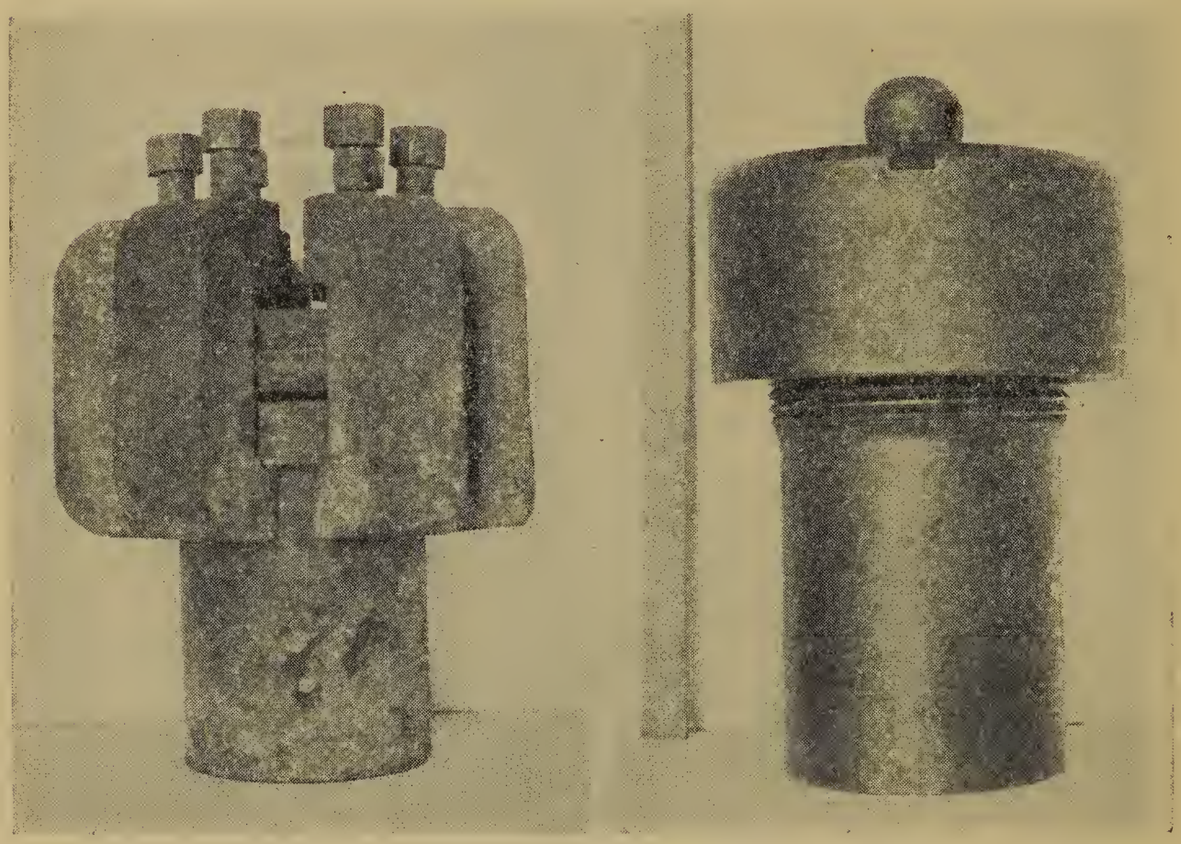

Fig. 1. Fig. 2.
Bombs Used in the Reduction of Rare Metal Chlorides.

The second bomb had a capacity ten times that of the first small bomb. It had an outside depth of 16.5 cm. (6.5 in.) and an inside depth of 12.7 cm. (5 in.) and outside diameter of 10 cm. (4 in.) and an inside diameter of 7.6 cm. (3 in.). The flange at the top was 12.7 cm. (5 in.) in diameter. The lid, which was 5 cm. (2 in.) in depth, was compressed upon the lower cylinder as before, with an intervening copper gasket, and maintained in position by six stout braces 3.8 x 4.4 cm. (1.5 x 1.75 in.) cross section and 15.2 cm. (6 in.) long. Each of these braces was

bolted down by 1.9 cm. (0.75 in.) bolts, 7.6 cm. (3 in.) in length. This bomb was calculated to withstand a total internal pressure of 36,400 kg. (80,000 lb.). This bomb has already been described in the references given. A picture of the bomb is reproduced in Fig. 1.

The operation involved in closing and opening the second bomb would be a somewhat laborious undertaking, if the experiment had to be repeated many times. A third type of bomb, much simpler in construction and quite as effective in operation has been designed by L. E. Barton of the Titanium Alloys Mfg. Co., and was used in some of our later experiments. This bomb is illustrated in Fig. 2. The cavity in the cylinder is closed by a slightly tapered plunger, which is held in position by the heavy cap, which is threaded on the outside of the cylinder. The copper gasket is rendered unnecessary by this construction and the chief source of weakness in the earlier bombs is thus entirely removed.

A larger bomb has since been constructed by the Titanium Alloys Mfg. Co., embodying the same principle in maintaining a tight joint between the lid and cylinder by means of perfect contact between two steel surfaces carrying a slight film of oil. In this larger bomb a five-pound batch of metallic material can be made.

OPERATION OF THE BOMB.

The operation of the bomb involves no novelty whatever. The requisite quantity of materials were introduced as rapidly as possible into the bomb. When the materials to be reduced were liquid below the reduction temperature, the sodium was introduced in large lumps. Where the materials were known to have melting points in excess of the reduction temperature the materials were introduced in successive laminæ with sodium. The bomb after closing was placed in a roughly constructed chamber built up of brick work and was heated by two blast lamps. The completion of the reduction was indicated by the sudden rise in temperature of the bomb. On cooling, the material remaining in the bomb was soaked with alcohol to remove traces of sodium

still unused, and finally washed with water and dried in alcohol and ether.

BERYLLIUM.

Beryllium oxide was extracted from beryl, and chlorinated after mixing with lamp black. The chlorination proceeded very slowly, and much time was required to produce enough chloride for reduction. When the oxide was converted to beryllium carbide under the electric arc, the chlorination proceeded much more rapidly.

The beryllium chloride was freed from iron by sublimation and transferred as rapidly as possible to the reduction chamber. In this way 88 g. beryllium chloride were reduced with 60 g. sodium. After reduction the contents of the bomb were washed free from sodium chloride. A considerable amount of a light blue-black flocculent precipitate was removed by levigation. The residue consisted of small rounded grains of beryllium. Most of the metal was found in the form of a semi-melted scoria, showing some signs of having been melted throughout the mass. The theoretical yield of beryllium was 9.8 g. Only 3.58 g. were recovered in the coherent form, a recovery of only 36 per cent.

The beads recovered from the reduction were found to contain 99.6 per cent beryllium. Some finely divided material contained only 84.8 per cent beryllium. On the assumption that the remainder is oxygen this gives as the composition of this residue 76 per cent beryllium metal and 24 per cent beryllium oxide.

The beads of pure beryllium possessed a silver-like luster and when cold could be flattened easily under the hammer.

The specific gravity of this material was 1.793. The melting point taken in hydrogen was found to be 1370° C. The beads of beryllium could not be burned completely in air, thus showing a considerable resistance to oxidation. They were readily brought into solution by hydrochloric acid, whereas in cold concentrated nitric acid the beads did not dissolve.

If large quantities of pure beryllium oxide or of beryllium chloride were available, there is no doubt that coherent metallic beryllium could be prepared by this method in considerable quan-

tity, thus giving an opportunity for the further study of this interesting metal.

CHROMIUM.

While chromium is not to be considered among the rarer metals it is not ordinarily met with in the pure condition. The violet chromium chloride can, however, be obtained commercially in reasonable amounts, and can be readily reduced by sodium to metallic chromium.

Of this chloride 350 g. were reduced by 154 g. of sodium. The largest pellet from the reduction weighed 11 g. The theoretical yield of chromium was 117 g. Sixty-seven grams of coherent metal were obtained, a recovery of 57 per cent of coarse metal. The material analyzed 99.86 per cent chromium.

On attempting to melt this material in the Arsem vacuum furnace the pellets showed signs of fusion but did not melt together. An analysis of the material after this heat gave 97.3 per cent chromium. Obviously the metallic chromium reduced the residual carbon monoxide in the furnace.

The specific gravity of the pure chromium was found to be 6.29 and 6.40 in two experiments. The metal is insoluble in hydrochloric or sulfuric acid in the cold, but dissolves readily in either when hot. In nitric acid the metal remains unatatcked.

The pellets could be forged readily when hot, the material thus behaving in a manner identical with titanium.

URANIUM.

The reduction of metallic uranium by sodium was first carried out by Peligot in 1869. Attempts at obtaining the metal in coherent form by this method, using large quantities of the material, were not successful.

In one experiment 308 g. uranium chloride (UCl_5) were reduced by 120 g. sodium. The theoretical yield is 177 g. Since 167 g. of metal were recovered the yield is 94 per cent. The metal is produced in powder form only, no coherent metal being obtained.

In a subsequent experiment, using larger quantities of material,

prepared through the courtesy of the Standard Alloys Co. of Pittsburgh, some small metallic beads were found in the resulting product. These beads could be rolled cold to thin sheets and could be forged with ease. An attempt at annealing the cold rolled material in the air resulted only in burning up the metal completely.

The fine powder prepared by this method is readily oxidized in air. One sample which analyzed 99 per cent uranium was found a year later to contain 89 per cent. The color had meanwhile changed from dark grey to green, indicating the formation of uranium oxide.

VANADIUM.

The metal vanadium has been recovered from the tetrachloride and trichloride by reduction with sodium. Its preparation from the liquid tetrachloride is difficult by reason of the great pressures which are developed in the bomb, due probably to the decomposition of the tetrachloride under the effect of heat. The solid trichloride can be reduced without difficulty.

Seventy-two grams of the liquid tetrachloride gave 11.87 g. vanadium on reduction, a recovery of only 63 per cent. On the other hand 38 g. of the trichloride gave 11.67 g. of residual metal, a 93 per cent recovery. The powder obtained contained 95 per cent of vanadium metal. No coherent grains of vanadium were obtained showing that the heat of reduction was not sufficient to melt the metal from the small amounts of material used. If carried out on a larger scale the pure metal could undoubtedly be obtained in coherent form. The specific gravity of the powder obtained was found to be 5.97.

In a subsequent run in which 92 g. of the mixed trichloride and dichloride were used, 37 g. of vanadium powder were prepared. The specific gravity of this material was found to be 5.53.

ZIRCONIUM.

Zirconium chloride can be readily reduced by sodium. In one experiment 324 g. of the chloride were reduced to zirconium metal. The theoretical yield is 126 g. Of this amount 96 g. of metal only were obtained, a yield of 76 per cent. The material was found to contain 93.2 per cent zirconium. The specific gravity of the product was found to be 5.29.

Zirconium has also been prepared by the reduction of potassium zirconium fluoride (Berzelius' method). Five hundred and twenty three grams of the double fluoride were reduced by 150 g. sodium, giving 174 g. of an air dried metallic product containing 95.9 per cent of zirconium metal. A second run on the same amount of material gave 43 g. of a coarse product analyzing 96.2 per cent of zirconium and 107 g. of fine powder analyzing 97 per cent zirconium.

No large coherent pellets were obtained in either case, the heat of reduction not being sufficient to melt the metal. Subsequent attempts to melt the powder have met with no success, so that it is impossible at this time to indicate whether the metal is malleable at high temperatures.

L. E. Barton, of The Titanium Alloy Mfg. Co., has succeeded by using larger quantities of material in reducing the chloride of zirconium to coherent metal. As yet however no further work has been done on this material.

SUMMARY.

The reduction of the pure anhydrous chlorides of the rarer metals seems to offer the best means of obtaining the metals in the pure condition. This method of reduction, which has been used by many observers in the past, has been used for the preparation of beryllium, chromium, uranium, vanadium and zirconium.

In the reduction of chromium and zirconium we have been assisted by R. H. Brown and A. R. Galloway, to whom our thanks are due.

Renssalaer Polytechnic Institute,
Troy, N. Y.,
March, 1923.

DISCUSSION.*

F. M. Becket[1]: Recent work by Mr. Cooper, of Cleveland, has shown that zirconium can be made relatively pure in a thoroughly fused condition, up to between 98 and 99 per cent zir-

* In the absence of the authors the above paper was presented by Colin G. Fink.

[1] Chief Metallurgist, Union Carbide and Carbon Corp., New York City.

conium. In the case of zirconium and some of the other metals here mentioned, greater purity has been obtained by electrolytic processes than by the reduction of the respective metallic chlorides by sodium.

H. K. RICHARDSON[2]: The authors do not give the percentage of uranium in the beads. A small percentage of iron will materially change all the characteristics of an alloy. While you can forge uranium containing a small percentage of iron, no 100 per cent pure uranium has been available for that test.

[2] Westinghouse Lamp Co., Bloomfield, N. J.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

AN ELECTROMETRIC METHOD OF FOLLOWING CERTAIN INORGANIC HYDROLYTIC REACTIONS.[1]

By George S. Tilley[2] and Oliver C. Ralston[3]

Abstract.

The use of the air electrode has been investigated for the purpose of following hydrolytic reactions, such as the removal of ferric iron and aluminum from copper sulfate solutions by various basic substances like powdered limestone, copper oxide, etc. Changes in direction of the voltage-time curve, or of the voltage-hydrolyzing agent curve, allow of following the process without the need of chemical analysis. The method likewise applies in the purification of zinc sulfate solutions and of aluminum sulfate solutions, and can be extended to other similar problems.

This paper deals with the use of the air electrode in following the course of a number of hydrolytic reactions that are of considerable commercial significance. The problem in connection with which the electrode was first used was in the purification of copper sulfate electrolytes by removal, through hydrolysis, of ferric iron, alumina and any other impurities that tend to hydrolyze at higher hydrogen ion concentrations than does copper. The hydrogen electrode fails in oxidizing solutions. On the other hand, solutions in practice are usually saturated with air, and they are frequently pumped or agitated with air, so it seemed desirable to follow the course of the hydrolysis by the help of a modified oxygen electrode, in which air is used for supplying the oxygen. The potential of this electrode toward the solution

[1] Original manuscript received January 31, 1923. Published by permission of the Director, U. S. Bureau of Mines.

[2] [3] Asst. Physical Chemist and Superintendent, respectively, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, Calif.

is a function of the hydroxyl ion concentration of the solution. The end-point of the hydrolysis was very sharp when this electrode was used as an indicator, and other characteristic changes in the voltage-time curves or voltage-titration curves made it possible to follow the changes in the solutions without the need of chemical analysis. The same method was later tried for following the hydrolysis of impurities in zinc sulfate solutions, as now used in electrolytic zinc practice, and for the removal of iron from solutions of aluminum sulfate and alum. In all cases satisfactory results were obtained.

This work was accompanied by a more or less systematic investigation of the limitations of the oxygen electrode, but several recent papers by Furman[4] and by van der Meulen and Wilcoxen[5] have covered this subject quite well, so we need not do more than emphasize the most important limitations. At first we referred potential measurements to the normal calomel half cell, but later used bi-metallic electrodes somewhat like those of Willard and Fenwick[6]. We retained the platinized platinum for the air electrode, but substituted other insoluble metals for the calomel half cell. Tungsten, molybdenum, tantalum and similar metals were used, and a later paper will report the results of this work. For the purposes which we desired, these metallic electrode pairs give sufficient difference of potential, supposedly due to differences in the solubility of oxygen in the electrodes, to follow changes in hydrogen or hydroxyl ion concentrations of solutions. All the curves given in the present paper were made with the calomel half cell for reference.

The oxygen (and the air) electrode is a capricious thing, which has caused much trouble to its investigators, and it still needs considerable investigation. It is unreliable for absolute hydrogen ion (or hydroxyl ion) measurements, because it shows a slow but steady drift, thought to be due to the formation of platinum oxides. It can be empirically calibrated for rough approximations of hydroxyl ion or acid concentrations. An example of such an empirical curve is given in Fig. 1.

One trouble with the oxygen electrode is the uncertainty as to whether it is a true oxygen electrode (which would make its

[4] Furman, N. H., J. Am. Chem. Soc. 44, 2685 (1922).
[5] Van der Meulin and Wilcoxen, J. Ind. and Eng. Chem. 15, 62 (1923).
[6] Willard and Fenwick, J. Am. Chem. Soc. 44, 2504 and 2516 (1922).

potential a function of the hydroxyl ion concentration), or a hydrogen peroxide electrode, whose potential is determined by the combination of hydroxyl ions to form hydrogen peroxide. It probably is a combination of the two, because its potential is greatly affected by the concentration of both oxidizing agents and hydroxyl ions. Fig. 1 shows the effects of change in hydroxyl

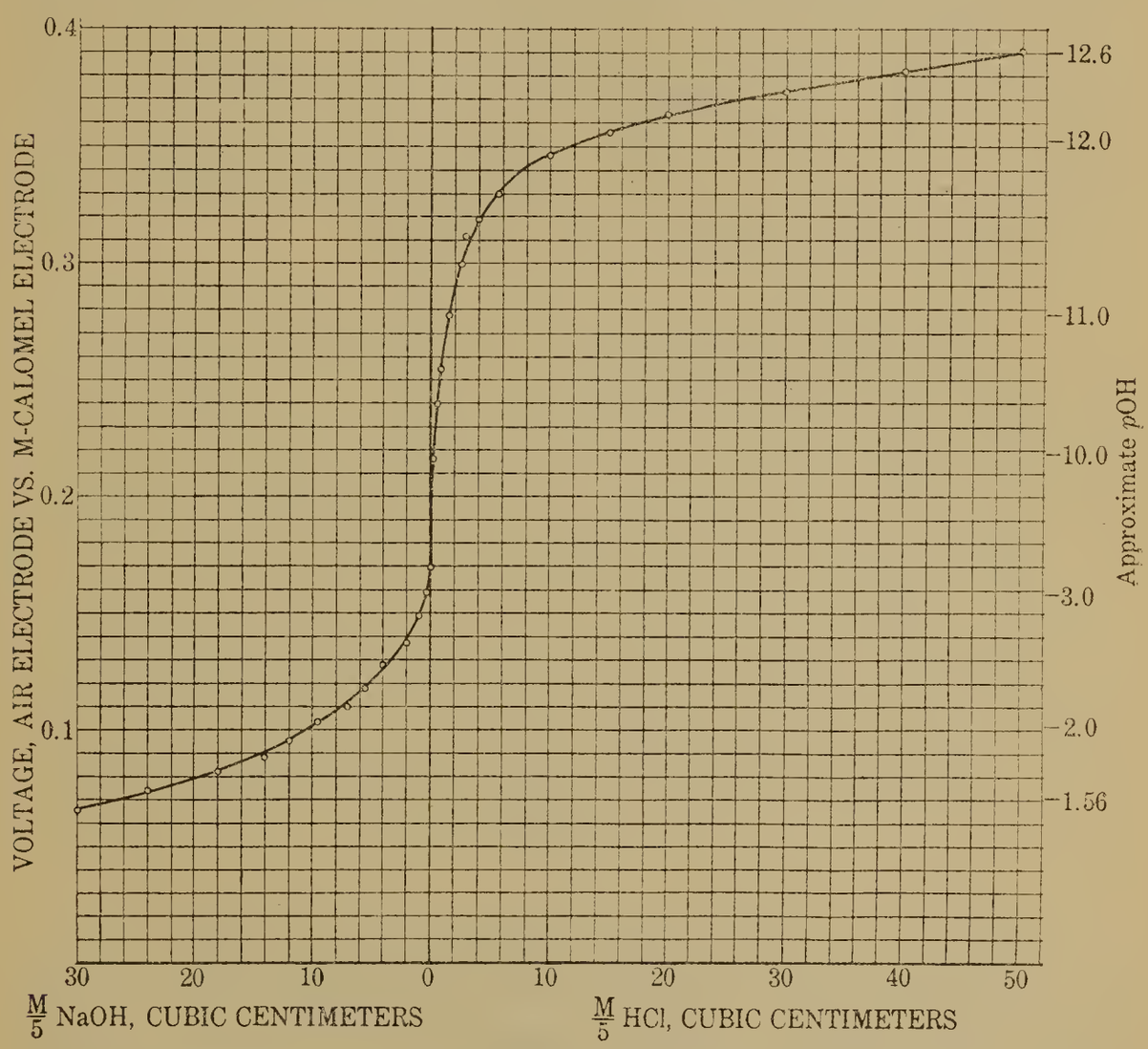

Fig. 1.

Concentration-voltage curve, air electrode in solutions of acid or alkali. Curve made by joining two curves, each made by starting with 200 cc water, and adding the amounts of acid or alkali shown in the figure. The approximate pOH for the concentrations corresponding to voltages given are shown separately. Voltage vs. calomel electrode, M/1 KCl.

ion concentration. The addition of hydrogen peroxide to solutions also causes marked changes in the potential of the electrode, and other oxidizing agents can likewise be titrated, as shown by Furman, using the oxygen electrode as indicator.

Due to the variability and unreliability of the air electrode, we have not tried to make measurements of the hydrogen ion

concentration, but have merely used it as an *indicator* of the beginning or end points of hydrolytic reactions. Its value lies not in the absolute potentials measured, but in showing a large change in potential when the end point of a reaction is reached.

The air electrode used by us consists of 1 sq. cm. of platinized sheet platinum welded to a platinum wire, which is sealed through a glass supporting tube. A normal calomel half cell was used for comparison, and frequent checks against a standard Weston cell were made. A Kohlrausch bridge, connected with a 4-cell Edison storage battery, and a galvanometer are connected to balance the unknown potential difference between the air and calomel electrodes against a known potential.

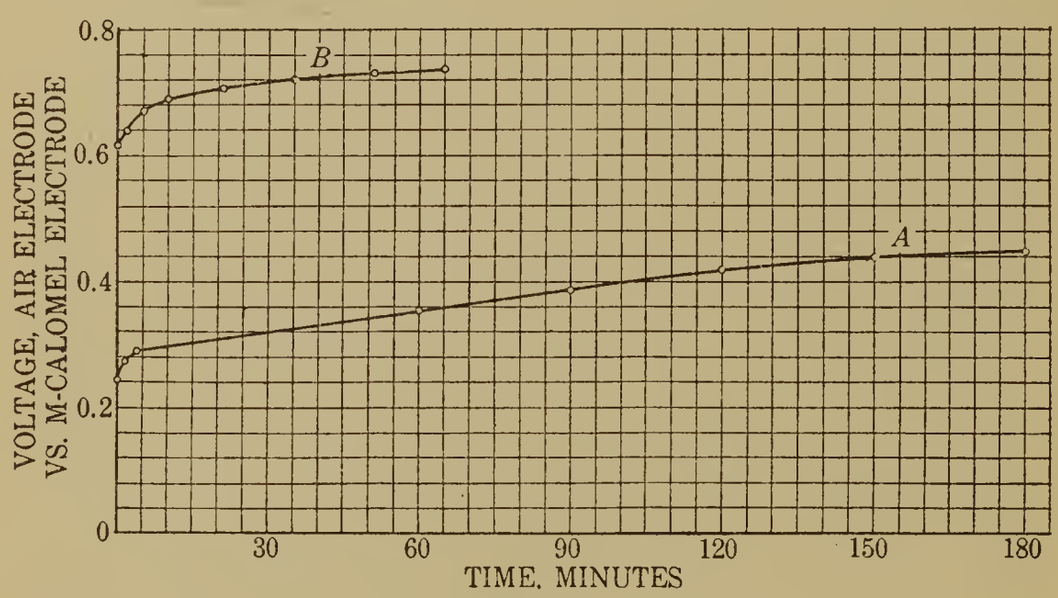

Fig. 2

In Fig. 2 are two curves obtained during the oxidation of ferrous sulfate to ferric sulfate by air and manganese dioxide in a slightly acid solution. Curve A applies to the discarded leaching solution of the Mountain Copper Co., of Martinez, California, where a copper-bearing pyrite cinder is leached with sulfuric acid, the copper precipitated on scrap iron and the solution discarded. The zinc content of this solution would be of interest if the iron could be economically oxidized and then removed by hydrolysis. The solution contained the following:

	g./L.
Cu	0.19
FeO	13.9
Fe_2O_3	nil
Zn	5.2
H_2SO_4	2.45

Manganese dioxide amounting to 10 g. per L. was added, and the solution was aerated for 3 hr. in a glass tube with a false bottom of canvas, through which the air was blown in order to make fine bubbles. Curve A is the curve of voltage plotted against time. As the curve flattened out the analysis of the solution showed the ferrous iron content approaching zero. Without the presence of the manganese dioxide the oxidation is slower, but other work, which will not be discussed here, has shown that a large portion of the oxidation of the iron is due to air, and most of the manganese that goes into solution is later hydrolyzed when the ferric iron is hydrolyzed by use of zinc oxide or calcium carbonate.

Curve B is for a similar oxidation of a solution made by decomposing a ferruginous clay with strong sulfuric acid. The higher acidity of the resulting solution makes the curve stand much higher on the diagram due to the higher voltage of the electrode. Manganese dioxide was also added in this case, and due to the strong acidity it was quickly attacked by the acid so that the curve began to flatten earlier than in the other case.

In Fig. 3 is a typical curve for purification of a copper sulfate solution, containing ferric and ferrous iron and some free acid over that necessary to prevent hydrolysis. In this case finely powdered limestone was added slowly in small amounts to study the effect on the voltage and sufficient time was given it to react before more was added. Curve C is divided into three zones. In zone A the free acid was first neutralized. The liquor was contained in the above mentioned glass tube, with a canvas diaphragm in the bottom through which air was admitted in small bubbles, and the air and calomel electrodes were introduced into the pulp near the top of the tube. The calomel electrode itself was outside the apparatus, but it was connected by means of a salt bridge with filter paper plugs to the interior of the agitation apparatus.

Due to inability to stir in the limestone with perfect smoothness, the curve in zone A is jagged. Here the first reaction was to neutralize free acid. When enough had been neutralized to allow ferric iron to hydrolyze, the pulp began to show the brown color of ferric hydroxide or basic ferric sulfate precipitates. Finally, when most of the ferric sulfate had been hydrolyzed, the addition

of further powdered limestone was sufficient to precipitate immediately all remaining ferric iron, and then lower the hydrogen ion concentration (and with it the voltage) to the point where the next salt in the solution (copper sulfate) would begin to hydrolyze.

This sudden lowering of the hydrogen ion concentration, with the corresponding increase in hydroxyl ion concentration, is in zone B. The addition of limestone was therefore stopped. The decreased hydrogen ion concentration is favorable to more rapid

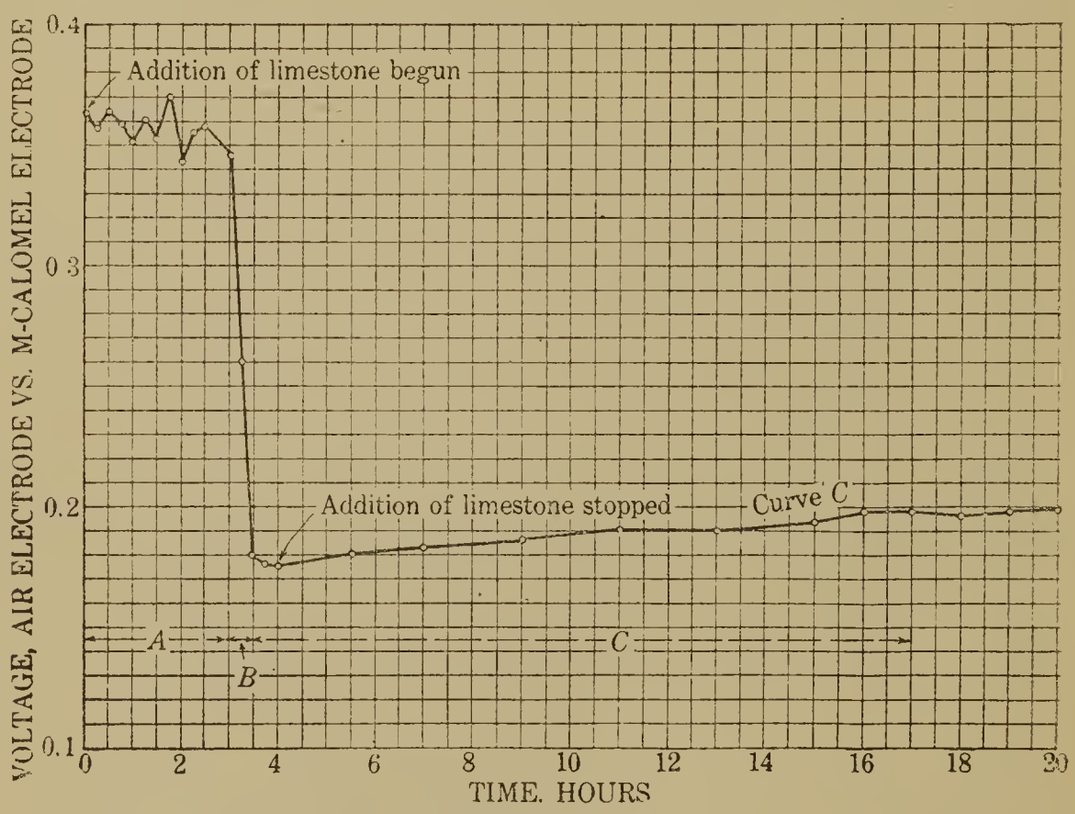

FIG. 3.

oxidation of ferrous sulfate solution by air, and in zone C it was found that the ferrous iron was slowly being oxidized and the voltage rose slightly. The length of time necessary for this oxidation varies with the amount of ferrous iron in the solution, and the curve frequently reaches a flat place, or a nearly flat one, before all the ferrous iron is oxidized. The electrode, therefore, is not a good indicator of the end of the oxidation of the ferrous iron, in case the oxidation is very slow.

Due to various inconsistencies in our work, other methods of following the reactions in the above type of work were tried.

In Fig. 4 are several curves comparing these voltage changes with other physical changes in the pulp. A sulfate solution was made up containing:

	g./L.
Ferrous iron	5
Ferric iron	5
Aluminum	10
Copper	30
Sulfuric acid	15

Limestone for hydrolysis, ground to pass 80-mesh.

Our work showed that all the ferric iron could be caused to hydrolyze when only about 70 per cent of the theoretical quantity

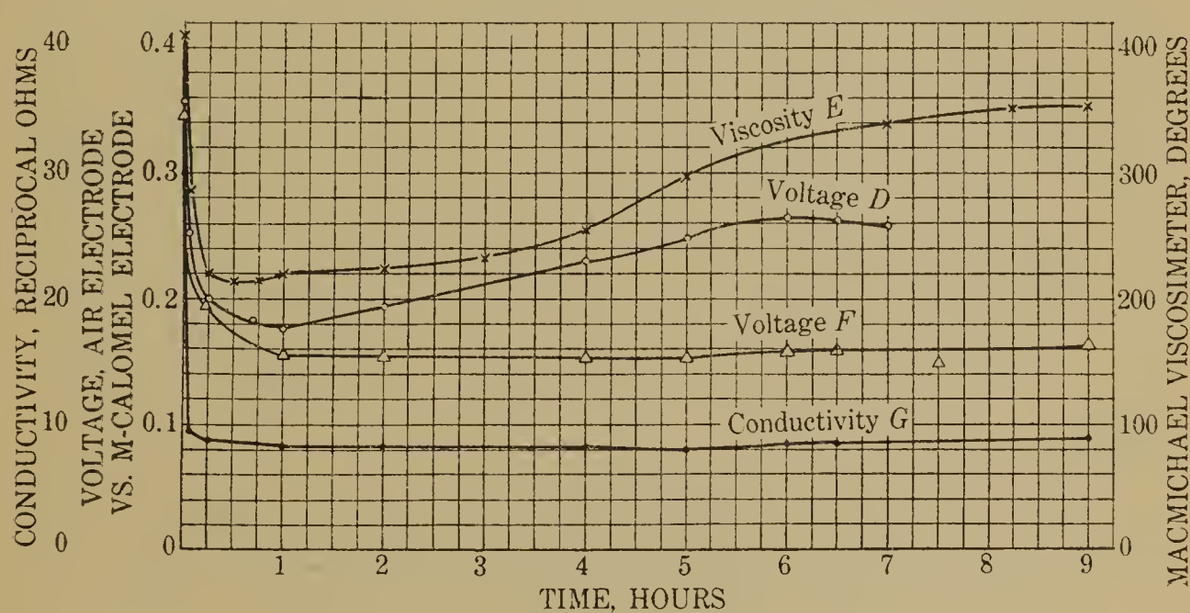

FIG. 4

of limestone equivalent to it had been added. Curves D and E are for solutions where the amount of limestone added corresponded to the excesss acid and to only 84.6 per cent of the total bases exclusive of the copper. Curve D gives the voltage-time curve after the limestone was added and curve E gives the viscosity-time curve after limestone was added to the solution in a Macmichael viscosimeter. Evidently some profound change is taking place in the pulp after all the ferric iron is hydrolyzed, and while the ferrous sulfate is being oxidized. Curves F and G are likewise a comparison of the voltage and the conductivity of

the pulp, but in this case only 74.4 per cent of the limestone equivalent to the total bases exclusive of copper was added. Evidently the conductivity follows the same variations as the potential of the air electrode.

The precipitate of calcium carbonate and the hydroxides of iron and aluminum contained very little copper when less than the theoretical amount of limestone was used for removing iron and aluminum, the copper content varying from a few tenths of one per cent to as much as 3 per cent. However, when 100 per cent of the theoretical amount of limestone was used the precipitate would contain 20 to 35 per cent copper. Evidently the first precipitate formed contained the iron, and probably the aluminum, in the form of a basic sulfate rather than as hydroxide. Part of the limestone could function in the precipitation of copper, unless it were restricted to the amount necessary to precipitate the other bases alone. When a sample of the pulp was filtered while passing through zone B of Fig. 3, or shortly thereafter, the filter cake consisted of white calcium sulfate, and the solution came through with the appearance of coffee, due to colloidal iron compounds. This colloid could be coagulated by heat, by long agitation in the presence of the other solids or by addition of more alkali.

At first we were inclined to ascribe the rise in voltage of zone C, Fig. 3, to oxidation of the ferrous salt by air, in comparison with the rise in voltage shown in the curves of Fig. 2. However, it is to be recalled that the hydrolysis of ferric sulfate at this hydrogen ion concentration is very rapid, and practically no ferric iron could exist in solution. As fast as the ferrous sulfate oxidized the iron would be precipitated. Besides, it was observed that the complete removal of ferrous iron did not necessarily coincide with the flattening of the curve.

The only other thing that was known to be happening in this zone was the coagulation of the basic ferric colloid. A rise in voltage could come from the increase of oxidizing agents in the solution or from an increase in acidity. Since soluble ferric iron probably was not present, and the colloidal ferric iron was being

coagulated, it was thought worth while to see if the increase in voltage was due to rise in acidity.

About this time the work of Tian[7] on slow hydrolysis came to our attention. He had followed the evolution of these colloids, and found it was a case of slow hydrolysis of their particles with release of acid and the formation of the coagulated hydrates. Our colloidal basic metal sulfates are therefore only intermediate stages in the reaction.

Viscosity-time curves that were exactly similar to ours were obtained by Gann[8] when dealing with the slow coagulation of aluminum hydrate.

We, therefore, felt justified in assuming that in zone C of Fig. 3 not only was ferrous iron being oxidized by the air, but the colloidal basic sulfates of iron and aluminum were being slowly hydrolyzed and coagulated, with liberation of sulfuric acid, and our experience showed that when the voltage rise began to diminish markedly the pulp could be easily and cleanly filtered. Any agitation beyond this point would be merely for the oxidation of the ferrous iron by air, providing any is left in the solution at the time of filtering.

To sum up what was done: The purification of a complex metal solution by selective hydrolysis was shown to be possible, if the hydrolyzing agent were added during agitation till the voltage of an air electrode showed a sudden marked drop. This amounts to electro-titration on a commercial scale, but the advantage of it lies in the ability to work without the use of chemical analysis. Also, due to the fact that less hydrolyzing agent than is equivalent to the metals precipitated was called for, it is simpler to add the reagent, using the air electrode as an indicator, than to try to calculate in advance the amount of reagent needed. The various changes in direction of the voltage-time curve all have their significance and can be usefully employed.

The removal of iron from zinc sulfate solutions, by use of either zinc oxide or calcium carbonate as hydrolyzing agent, was

[7] Tian. J. chim. phys. 19, 190 (1921).
[8] Gann, Koll. Beihefte, 8, 64 (1916).

exactly similar to the above work on copper sulfate solutions. The only requirement is that the ferrous iron be oxidized to the ferric stage as ferrous iron will not hydrolyze until after most of the other bases have been precipitated.

The order in which some of the various common metals begin to hydrolyze from their sulfate solutions, with approximate hydrogen ion and corresponding hydroxyl ion concentrations at which they begin and end hydrolysis, is about as follows:

	H^+ ion	OH^- ion
Silicic acid	10^{-2}	10^{-12}
Titanium	$10^{-2} - 10^{-3}$	$10^{-12} - 10^{-11}$
Ferric iron	$10^{-3} - 10^{-4}$	$10^{-11} - 10^{-10}$
Aluminum	$10^{-4} - 10^{-6}$	$10^{-10} - 10^{-8}$
Manganese (ous)	?	?
Copper (ic)	$10^{-6} - 10^{-6.5}$	$10^{-8} - 10^{-7.5}$
Zinc	$10^{-6.5} - ?$	$10^{-7.5} - ?$
Water	10^{-7}	10^{-7}
Ferrous iron	$10^{-9} - ?$	$10^{-5} - ?$

Calcium carbonate, in equilibrium with the carbon dioxide resulting from its hydrolysis when suspended in water gives the solution a concentration of hydrogen ions between that of zinc solutions and water.

An interesting thing about this series is that it is somewhat like the electrochemical series of metals, in that the precipitate of hydrate or basic salt of any one in the series will react with a solution of any metals above it in the series, precipitating that metal and going into solution itself. Also, like the electrochemical series, this rule does not apply if the two metals are too close to each other in the series. For instance, the aluminum precipitates of hydroxide or basic sulfate will not remove ferric iron from the solution, but calcium carbonate can be slowly added to a solution containing ferric iron and aluminum and throw out the ferric iron almost completely before the precipitation of much aluminum.

We have studied the purification of aluminum sulfate solutions made by reacting on clay with sulfuric acid, and have been able to remove separately, first a precipitate containing the silica and

titanium, then a precipitate containing the ferric iron, and leave a clean solution of aluminum sulfate. Iron-free alum can be prepared in this way, and the operation is simple and inexpensive. We were able to avoid filtration or even sedimentation by choosing the exact voltage (determined empirically by varying the conditions) at which the iron would precipitate as a colloid in the cold solution, but would remain in true solution while hot.

By bringing a very strong solution of alum to this particular hydrogen ion concentration (using limestone for reducing the acidity), the alum would crystallize during cooling, and the iron would form a colloid which remained in the mother liquor, and on centrifuging the iron passed out of the system with the mother liquor, leaving only such colloid as was associated with the mother liquor sticking to the crystals. This could be washed off with a clean solution of iron-free alum. Other possible modifications have been studied and will later be reported.

The air electrode is now used as an indicator in a number of otherwise difficult determinations in our laboratory, most of which have been discussed in recent literature or will be reported later by us.

DISCUSSION.*

M. R. THOMPSON[1] (*Communicated*): Unpublished results obtained at this Bureau by the indicator method lead to the conclusion that ferrous iron begins to hydrolyze in a faintly acid solution (probably pH 5 to 6); rather than in a faintly alkaline solution (pH 9) as is here suggested. Consideration of this fact may be of interest in the application of the method of Tilley and Ralston to the treatment of solutions.

It is suggested that the reason that the hydrolysis of a heavy metal occurs over a wide range of hydrogen ion concentration,

* In the absence of the authors the above paper was presented by Wm. Blum.

[1] Chemist, Bureau of Standards, Washington, D. C.

rather than in a narrow range, may be partly due to adsorption of the added reagent by the precipitate.

LEON MCCULLOCH[2]: How can the hydrogen ion concentration of a solution containing both ferrous and ferric salts be measured?

W. BLUM[3]: It is not possible by means of a hydrogen electrode except in very dilute ferric solutions and then only by the use of special precautions. [Broune, J. Am. Chem. Soc. **45**, 299 (1923).]

[2] Research Dept., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[3] Chemist, Bureau of Standards, Washington, D. C.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

THE EFFECTS PRODUCED BY AGING IN SYNTHETIC RESIN MOLDED PRODUCTS OF THE PHENOL-FORMALDEHYDE GROUP.[1]

By E. J. Casselman [2]

Abstract.

In commercial forms of molded phenol-formaldehyde resins, these bodies are used as binders for fibrous materials, such as paper, cloth and the like. Looked at from another standpoint, the fibers are present as structural reinforcing agents.

The synthetic resinous binder in its commercial form is marked by the presence of certain impurities, most of which are of a volatile nature. During aging the escape of these impurities is the principal feature, and it is accompanied by slight changes in the electrical and mechanical properties of the body.

CHEMISTRY OF THE FORMATION OF THE RESINS.

The products of which I am speaking consist of a fibrous material, such as paper, duck, or asbestos, firmly bound together and impregnated with a resinous body. They go under the trade names of micarta, dilecto, formica, celeron, etc. The particular resinous body to which I refer is the class of compounds formed by the reaction of approximately one molecule of formaldehyde upon one molecule of phenol. These bodies have the well-known trade names of bakelite, redmanol, condensite, etc. They began to come into commercial use about fifteen years ago. There are many ways of forming these resins, some of which are quite direct, and others for special purposes are somewhat indirect. While

[1] Manuscript received June 15, 1923.

[2] Research Lab., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

it is not part of my purpose to compare any of these materials as marketed under the various trade marks, it is my purpose to consider the most common commercial forms and no others.

Pure phenol and pure formaldehyde react very slowly even when heated. Under the influence of catalytic agents, especially alkaline bodies, a combination takes place quite rapidly. It is probable that several types of combination between these raw materials are taking place simultaneously. Some of the journal literature and patents lay stress upon the formation of saligenin or hydroxybenzylalcohol as the initial product of the main reaction. This may be true when acids are used as the catalytic agent, or such an alkali as sodium hydroxide, but commercial processes generally use ammonia. When ammonia is first added to such a mixture as equimolecular parts of phenol and formaldehyde, it first reacts with the formaldehyde to produce haxamethylene tetramine, and the reaction is between this body and the phenol. We know from the chemistry of the reaction between anhydrous phenol and hexamethylene tetramine that complex compounds like hexamethylene tetramine triphenol are among the intermediate compounds, and the presence of water probably does not prevent the formation of some of this material, even if it also causes the formation of saligenin. The obscurity of the chemistry of the condensation process does not prevent our observing that a distinct stage is reached when most of the original formaldehyde and phenol have disappeared, and a resin is present which is fusible and soluble in many organic solvents, soluble in alkali, insoluble in water and acids.

This resin has the peculiar property of undergoing further change under the influence of heat. It goes through several stages of decreasing fusibility and solubility until, when it has reached an equilibrium state, it has the well-known properties of being infusible at all temperatures below its charring point, insolubility in all known reagents, greater strength than any other known resin, and electrical insulating properties of a high order. The chemistry of this change is likewise obscure, but it consists of a polymerization of some kind, and the product has the ultimate chemical composition of C = 75.4 per cent, O =

18.7 per cent, H = 5.9 per cent. Some writers have defined stages of the condensation and subsequent polymerization, but it is an open question whether the changes are not all continuous, and the stages arbitrary.

METHOD OF MANUFACTURE OF MOLDED PRODUCTS.

It has been the policy of the companies owning the patents upon these resins to make the initial condensation themselves, and sell these initial products to other companies who fabricate them into their final form. In the case of laminated products, the initial soluble resin is dissolved in a suitable solvent, usually alcohol, or alcohol and small amounts of other solvents. This alcoholic varnish is then used by the fabricating company to impregnate paper, cloth, etc., and the paper is dried in a way to drive off the solvent. The treated paper is then cut into suitable sizes, stacked, and compacted in a hot hydraulic press until the final polymerization is complete, when the now compact board is cooled and removed from the press. During the hot pressing the resin has gone through all the stages of polymerization, first fusing and flowing around the fibers of the paper, then becoming infusible, and lastly having the properties of the completely cured resin.

The molded products as distinct from the laminated products are made from an intimate mixture of finely powdered initial resin and comminuted fibers. This mixture is loaded into molds and pressed hot under such conditions that the resin first fuses and flows around the fibers, then goes through its polymerization process until it becomes infusible and insoluble.

PROPERTIES OF THE COMMERCIAL PRODUCTS.

What is the difference between the binder in a sample of commercial micarta and the chemically pure resin I have described earlier? Why does it change during aging if it has been cured to a state of equilibrium? We need to know something more than the organic reactions involved to answer these questions. The main differences are due to the process of manufacture, and consist in the presence of impurities. One impurity present as

introduced during the initial condensation is ammonia, the catalytic agent. Although only small quantities are used in one process (a wet process), the last traces remain in the resin during all subsequent treatments. It can only be removed by a drastic heat treatment, for instance, 180° C. for even very thin pieces. In another process, which is an anhydrous one, large quantities of ammonia are used in the form of hexamethylene tetramine, but most of it is removed before the initial condensation product is dissolved for use as varnish, or ground for mixing into a moldable powder. In spite of serious attempts on the part of the manufacturers, some ammonia is left in the resin, and this remains either chemically combined or in some state of solid solution, in the finally cured product. Since some of the users of the laminated fiber sheets have specified that the nitrogen content shall be less than 0.2 per cent, commercial sheets are usually within this limit, but it is true that more ammonia is present in the materials made by the dry process than in those made by the wet.

Another major impurity is uncombined phenol or cresol, introduced as one of the initial ingredients. None of the commercial processes has produced a resin that does not contain some free phenolic body even when completely cured. It is too much to expect an organic reaction to go to completion. It is too much to expect all the phenol to react with all the formaldehyde, even when the initial proportions are exactly correct. The formaldehyde being volatile, the small fraction of it which remains uncombined due to incompleteness of reaction escapes before the final curing. The phenol being much less volatile remains with the resin, and some of it is always present after the complete curing of the body. It would be possible, of course, to devise a method which would eliminate the free phenolic bodies as well as the formaldehyde in the early stages of the condensation, so that they are not present in the end-product. It has not seemed necessary or desirable to do so, as small amounts of phenol have no deleterious effects upon the product, and it aids in making the resin flowable in the hot press.

Another major impurity is alcohol or benzol, used as solvent for the varnish. When paper or cloth impregnated with this

varnish is passed through a heated tunnel it is possible so to regulate the conditions that only a part of the solvent is driven off, but all of it may be driven off. If the attempt is made to drive it all off, however, the resin remaining on the paper is likely to flow with greater difficulty when it is hot pressed later, than if a very small portion of solvent is left in it. Furthermore, there is some chance that a slight curing may take place on the surface layers which will prevent fusing of the binder when the sheets are stacked and hot pressed. For these reasons it is the practice of manufacturers to so dry the paper that a small amount of solvent remains with the resin. For most purposes this is harmless, and it remains with the fiber board even after it is cured.

Another impurity is water, which was originally present with the formaldehyde. Even if the resin as dissolved in the solvent is anhydrous, sheet paper or cloth is never entirely free from moisture, and the driving off of the solvent in the drying tunnel leaves traces of water behind in the same way that it does solvent.

The last impurity worth mentioning is oxygen and oxygen compounds of the phenolic resins. The order of magnitude of these impurities is much lower than that of the others I have mentioned. The oxygen may come from several sources, it may be introduced in fact at any time when the bodies are in contact with air before molding. The effect of oxygen upon a bakelite body is to oxidize it, forming a deep colored brittle infusible body, likewise resinous in nature. Whereas the original bakelite as made from phenol has a carbon content of about 76 per cent, the oxidized product has been so diluted by absorption of oxygen in the molecule as to have a carbon content of only 65 per cent. In the process of this oxidation water is also formed, probably by attacking a hydrogen atom of one of the ring structures. However, oxidation does not occur to any extent at temperatures below 100° C., and only begins to be rapid above 150° C.

The presence of these impurities can always be borne in mind, namely, a few tenths per cent ammonia, up to one or two per cent volatile matter, mostly water and alcohol, and an average of one and one-half per cent free phenolic body, and entrapped oxygen.

The effects of the presence of these bodies is easily understood. Ammonia and water together have some conductivity within the structure. This conductivity does not seem to affect the puncture voltage so much as the value known as the power factor. The puncture voltage is uniformly satisfactory on these materials, but the power factor may be as high as 0.5 per cent at ordinary temperatures.

The aging of these bodies consists largely in the gradual evaporation of the volatile impurities. Anyone with a mathematical turn of mind could get considerable pleasure deriving a formula for the rate of diffusion of the vapors out of the solid structure, depending upon the vapor pressure of each constituent, its concentration, the temperature, thickness, film effects, conditions of the external medium, etc. As a matter of fact the humidity of the air does affect the rate of weight loss considerably, and such a body in humid air may gain as much water from the air as it loses alcohol, phenol, and ammonia by evaporation. In the dry air of a hot climate a 0.15 cm. (1/16 in.) thick piece may lose up to 1 per cent of its weight in a few weeks, while a 2.5 cm. (1 in.) thick piece in this climate would be years changing its weight by 0.2 per cent. The disengagement of the last traces of ammonia requires heat, as pointed out before, but ammonia can usually be noted by its odor whenever these bodies are sawed, or when sawings are left standing in a bottle.

Some contraction in volume takes place when the vapors leave the body. A lineal contraction of as much as 2 per cent takes place in the resinous binder, but the figure is much less than this in the laminated structures because of the reinforcing effect of the fibers. The contraction in the direction of the laminations is not over 0.4 per cent, and usually is less than 0.2 per cent. A convenient formula to remember is "per cent contraction is 0.1 per cent wt. loss." The electrical properties are improved to the extent that the power factor drops from about 0.5 to 0.2 per cent after the aging process. These figures apply only to thin sheets, as thick sheets are so long in aging that no measurements have been made.

It is obvious that these effects are increased and accelerated by

heat. When micarta is used in a service where it is heated, the reaction of the entrapped oxygen is also of importance. Of course some reaction between the oxygen and the resinous binder has already taken place in the hot molding, in fact the color of the body in the absence of dyes is a measure of the temperature at which it was molded. The molding is only a short affair, compared to which service conditions may be very long. Misuse of a resinous body as regards temperature of service may result in its disintegration, part of which is due to oxidation and part to chemical decomposition.

The effect of this aging upon the hardness of the binder is best shown by scleroscope tests. In one sample that was observed the scleroscope hardness increased from 88 to 94 in a period in which the weight decreased 0.78 per cent. It is possible to obtain resins with a scleroscope hardness of 105 by appropriate heat treatment, but this never occurs throughout the whole body of the structure in any ordinary aging.

Specific data on aging are hard to interpret because of the dependence of the values upon so many variable factors, such as proportion of filler and paper, kind of paper, etc. I do feel justified, however, in presenting the conclusion that these resinous bodies do improve in electrical properties during aging, and other changes that occur are slight and of little significance.

DISCUSSION.*

E. E. Stark[1]: The products dealt with in this paper are interesting from a radio manufacturing standpoint, and their ability to withstand puncture is undoubtedly good. In making a rough comparison of the insulating qualities by a simple method of using the gold-leaf electroscope charged, and holding a bakelite rod in the hand by one end and the other end of the rod touching the electroscope, one can get a rough idea of its insulating qualities.

* In the absence of the author the above paper was presented by C. J. Rodman.

[1] Elyria, Ohio.

The result is disappointing in comparison with hard rubber or dry glass.

What was the method used in determining the power factor?

C. J. RODMAN[2]: In answer to what is power factor, even though it may seem to be a more or less peculiar way of expressing a physical property, it is, nevertheless, significant. It is the ratio of the watt loss as measured by the watt meter to the difference in potential times the current that passes. Loss of energy in this way in insulating materials, I think, is explained by the next paper, by Mr. Howes.

COLIN G. FINK[3]: Some time ago we made up acid cells with bakelite boards (10 per cent bakelite) and found that certain acids do not affect it appreciably for years.

H. B. WAHLIN[4]: I had occasion to use bakelite for insulation, and I found that by dipping the rods in sulfur so as to give them a coating, the resistance was increased quite appreciably. They could thus be used for work which requires extremely high insulation.

E. E. STARK: Would paraffin be just as good as sulfur?

H. B. WAHLIN: It does not have the insulating properties.

F. G. COTTRELL[5]: With reference to the sulfur, I recall a piece of work we had occasion to do a number of years ago, when we were studying possible uses for elementary sulfur. One of the main drawbacks to its use mechanically was the low tensile strength of cast sulfur, partly perhaps because of the gradual conversion of the monoclinic form, into which the sulfur first solidifies, to the rhombic, which is the stable form at ordinary temperatures. However, if you mold the desired objects under high pressure at room temperature directly out of flowers of sulfur you get an entirely different product. I have never actually measured its tensile strength, but I suspect it would be

[2] Research Lab., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[3] Head, Div. of Electrochemistry, Columbia Univ., New York City.
[4] Dept. of Physics, Univ. of Wisconsin, Madison, Wis.
[5] National Research Council, Fixed Nitrogen Res. Lab., Washington, D. C.

much higher than cast sulfur. The material has a far finer and more uniform texture with a fracture resembling the finest porcelain, and it machines beautifully.

C. P. MADSEN[7]: Some years ago we investigated substances which would protect hooks and connecting rods in the plating bath from deposition, and thought that bakelite would serve this purpose. We were surprised to find that a deposit in some baths took place on bakelite almost as readily as on anything else.

There is this serious drawback, *viz.*, that bakelite cannot be used in a nickel bath, particularly one containing chloride. We found after 12 hr. that although the immersion sample of bakelite gained in weight, the bath showed a phenol content which was injurious. Although it may have been phenol or a phenol compound, it was sufficient to know that it did not work.

H. C. P. WEBER[8]: I believe that with thoroughly cured bakelite, which one rarely obtains, this difficulty would not exist.

C. P. MADSEN: The bakelite we used was supposed to be thoroughly cured; it was of the light amber variety and was purchased directly for our purpose.

H. C. P. WEBER: Some of our data indicate that bakelite will lose material for 20 days. That may throw some light on the mysterious behavior that Mr. Madsen spoke of. Suppose the bakelite contains ammonia, and it is mentioned in this paper that bakelite chips and sawings, in a closed bottle, nearly always show ammonia vapor. If such material is placed in the bath there will be a deposit of hydroxide and then, of course, you are set for reduction followed by plating. However, I think that if those hooks were put in an oven at 100° and baked for a week different results might be obtained.

E. J. CASSELMAN (*Communicated*): I have never analyzed any commercial clear amber bakelite which did not contain from 5 to 10 per cent. uncombined phenol; neither have I been able to produce clear bakelite in the laboratory without using a similar

[7] Consulting Engineer, New York City.
[8] Research Lab., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

excess of phenol. The chances are that the clear bakelite used by Mr. Madsen, even though completely cured, contained large quantities of this impurity, and was, therefore, unsuitable for insulation purposes when submerged in aqueous solutions.

In the laboratory it is possible to prepare bakelite containing a very small excess of free phenol, which is at the same time clear and free from cracks, but I do not believe such phenol-free product is being marketed. A very pure resinous product is micarta. However, if Mr. Madsen had used micarta he would have gotten into other difficulties, on account of the greater water absorption rate of micarta.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

COMPOSITION AND AGING OF INSULATING VARNISHES.[1]

By H. C. P. Weber.[2]

Abstract.

It has been shown that during the drying and oxidation of varnishes, conducting materials are formed which produce appreciable lowering of the insulation resistance of electrical apparatus. Values are given to show that the amount of these "low resistance materials" is proportional to the amount of oil in the varnish, and that there is a noticeable difference in the amount produced by different oils. Linseed oil for instance yields these substances in much greater quantity than other varnish oils.

In a previous report to members of this Society it was shown that during the natural oxidation of oil varnishes for a period of time the resistance of a varnished insulation might decrease. This decrease in resistance is the result of formation, by oxidation, of low resistance materials, chiefly acids of lower molecular weight, which are volatile and form conducting solutions with water.

A number of factors markedly influence the amount of these low resistance materials, and in making examination of varnishes for insulating purposes the test must be made under fixed conditions to obtain comparative values. The results to be described were obtained by taking cotton strips, standard insulating tape, and dipping unit lengths of this tape (one meter) into the varnish and allowing them to drain. Under these conditions the average insulating varnish has become air dry in 48 hr., some of them in 24 hr., as is shown by the stoppage of weight loss due

[1] Manuscript received June 15, 1923.

[2] Research Lab., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

to evaporation and the physical condition of the tape. The various varnishes yield a varying quantity of varnish base, depending on the nature of the varnish. In carrying out the examination for acidity a check is therefore obtained on the rate of drying and the body of the varnish.

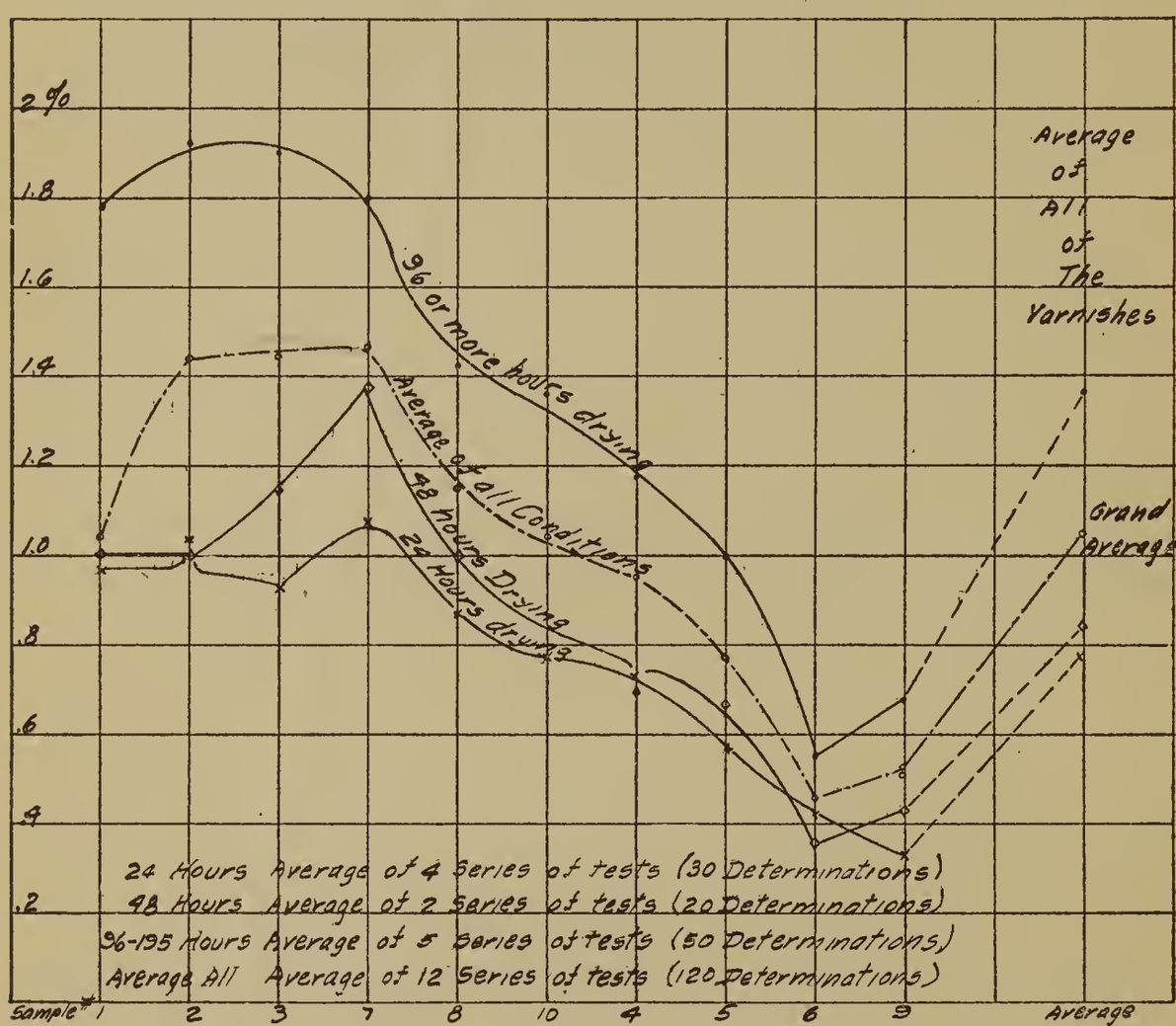

FIG. 1.
Average acidities, 10 varnishes, varying times.

Sufficient number of strips were prepared so that a sample could be taken on successive days over a period of time. Certain of the samples were exposed to the air at normal temperatures, while a corresponding number of samples were "baked" at 100° C. in order to obtain a comparison of the effects produced.

Fig. 1 indicates the progress of the formation of low resistance materials in 10 samples of varnish examined. The results for each period, say the 24 hr. period, are for a large number of determinations in which other factors than the time were varied. The results for each varnish are therefore average results.

Inspection of the curves shows two things. First, that the amount of acidity formed is really a function of the time, increasing as the oxidation progresses. Other values which are not included here indicate that for most varnishes the oxidation increases up to 96 hr., but after that it is practically complete, when the film is thin.

The second fact shown is that the values are really characteristic for the particular varnish. While the quantity increases with time, the order of the different samples remains essentially the same so that for purposes of comparison a 48 hr. test period is as good as a 96 hr. period.

The dashed line shows the average for all conditions and times; the value marked "grand average" indicating the averages of the ten samples again combined. This value shows that 1 per cent of water soluble acid can *normally* be expected to exist in an air dried varnish.

TABLE I.

Results of Drying and Baking Varnishes.

Material	Per cent Oil	Average per cent acid	
		Air dried Per cent	Oven dried Per cent
Linseed Oil A.....	80	2.4	2.34
B.....	80	3.3	3.00
C.....	80	3.5	3.02
Restrainer D.....	80	2.5	2.8
China Wood	80	1.5	1.8
Linseed	70	1.43	1.7
Linseed	50	0.88	1.68

The results in Table I were obtained on specially prepared samples of varnishes. There were over thirty samples of known composition and a large number of tests were made so that the average results quoted here give a reasonably accurate picture of the true relations. Under "material" the kind and percentages of oil used in preparing the varnishes are given. The values given under "baked" were obtained by baking for a short time (45 hr.) at 95° C. Continued baking would of course finally remove the

greater portion of low resistance materials. The initial effect is to hasten its formation.

Inspection of these results shows that as far as the oils are concerned: Linseed oil varnishes are the most acid. China wood oil varnishes develop less acidity than the linseed oil varnishes. With the same oil the acidity developed is greater the greater the percentage of oil.

DISCUSSION.

H. C. P. Weber: A breakdown in machinery of that kind may be due to a direct short circuit produced by low conducting materials.

The acidity that is formed is the result of natural oxidation of the varnish. It may accumulate in the insulating material and be distributed throughout the same. For instance, you have a motor and it runs hot, some part of it remaining cooler than the rest. What you do is to shift this material to the cooler portion where it accumulates. Soon you will have a short circuit there which will finally burn out the coil. This will affect the cold part of the motor.

Alex Lowy[1]: In the preparation of these varnishes do you use any stabilizer to counteract the acidity?

H. C. P. Weber: The trouble is that you want the varnish to oxidize. The other trouble is that the moment the varnish oxidizes the acid forms. The acid formation seems to be intimately connected with the oxidation of the varnish, so that if you were to prevent it, you would probably prevent the oxidation of the varnish. Whether you can put something in to take it up later, is a different proposition. I do not know.

[1] Professor of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 27, 1923, President Hinckley in the Chair.

EFFECT OF CONTINUED HEATING ON THE POWER FACTOR AND RESISTANCE OF IMPREGNATING COMPOUNDS.[1]

By D. E. Howes.[2]

Abstract.

A large number of field coil windings were impregnated with four kinds of compounds, and heated at temperatures 105°, 125° and 150° C. for a period of 120 days. At intervals the electrical condition of the insulation was determined by measurement of its power factor and resistance. Even though considerable oxidation took place, the electrical properties continued to improve throughout. The results show that continued heating at these temperatures, while it does not seriously affect the electrical properties of the insulation, does destroy its practical value, due to its mechanical deterioration.

In the construction of coils and windings for electrical apparatus usually some impregnating compound is employed. After the coils are wound they are impregnated and baked at a moderate temperature, to remove moisture and to cure more thoroughly whatever insulation is used in their construction. The impregnating compound serves as a mechanical support for the windings and also as an insulator between them. To perform this latter function well, it must be moisture-proof and in some applications oil-proof. It must have good penetration so that no air pockets will remain between the windings after impregnation, as they may cause insulation failure and thus short-circuits in the coils. In practice they may be subjected to elevated temperatures, and it was for the purpose of finding out how continued heating actually affected the insulating qualities of the impregnating compounds, that the investigation herein described was undertaken.

[1] Manuscript received June 15, 1923.

[2] Research Laboratory, Westinghouse Elec. and Mfg. Co , East Pittsburgh, Pa.

Field coils were wound on spools and each double layer had a wire extended and separated from the other layers. Thus, by connecting alternate groups to one terminal and the remainder

Fig. 1

to another terminal, a potential could be applied between layers. Part of the coils were wound with 0.081 cm. (0.032 in.) D. C. C. copper wire and the rest with 0.25 cm. (0.1 in) square wire. Fifteen coils were impregnated with each of the following com-

pounds. Bakelite varnish, No. 2 gum, No. 3 gum, and No. 35 gum, making a total of 60 coils. Bakelite is a familiar material. No. 2 gum is a flexible, moisture-proof gum with an asphalt base. It is not oil-proof and its drop point is 150° C. No. 3 gum is oil-proof and is hard and brittle. Its drop point is 110° C. No. 35 gum is brittle pitch obtained by the destructive distillation of hard woods. It is oil-proof and has a drop point of 118 to 125° C.

The coils were heated in thermostatically controlled electric ovens, and the electrical measurements were made at the heating temperature. A special switch in each oven permitted the coils to be placed in the testing circuit in turn without opening the oven.

The temperatures were 105° C., 125° C., and 150° C., and five coils of each kind of impregnation were maintained at each temperature. One series of tests was carried out for a period of 20 days. The coils were then duplicated, and a series of tests carried over a period of 120 days. Power factor was measured by an electrostatic wattmeter, and 220 v. a.c. was applied between layers. Power factor W/EI, where E is the voltage applied to the terminals of the coils, I the current passing through the insulation between layers, and W the watts consumed in the insulation as measured by the wattmeter. Power factor, then, is a measure of the rate at which energy is lost in the insulation when a voltage is applied, and the poorer the quality, the greater the power factor in general. Resistance was determined by applying 90 v. d.c. and measuring the current through the insulation with a sensitive galvanometer provided with an Avoton shunt. These measurements were made at intervals during the heating.

Curves have been drawn showing the variation of power factor and resistance with time of heating for each coil under test. These two electrical properties were chosen, because they indicate better than any other tests, the condition of insulation. As in general the characteristics were similar for all the coils, curves are shown for only one coil for each different temperature and kind of impregnation. An examination of Fig. 1 and 2 shows that the resistance of all the materials increases with the time of heating, and the higher the temperature the lower is the resistance. The resistance at room temperature was of the order of 1000 times as great as that at the oven temperatures. The resistance of the

bakelite impregnated coils was much greater than any of the gums and the power factor much less. This is because it does not soften.

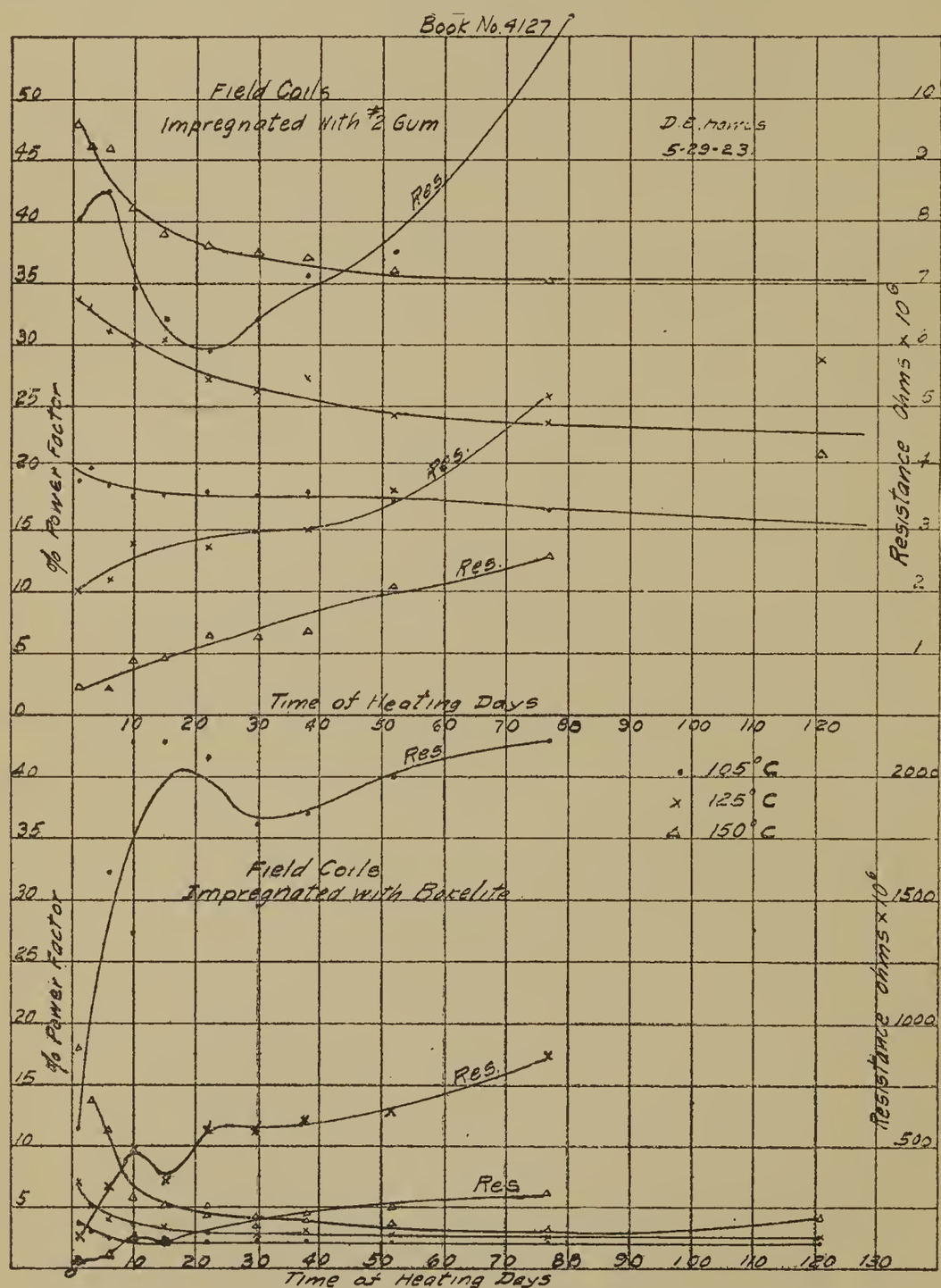

FIG. 2

In general, the power factor decreases quite rapidly for the first 20 days, and thereafter changes very little. Also at about 10 or 20 days, depending upon the temperature, there is, in some cases, a noticeable change in resistance. That is, it increases for a period, then decreases slightly, followed by a continuous increase.

This is particularly noticeable for the lower temperatures, and the time of heating that has elapsed before this occurs is less for the higher temperatures. This indicates a final stage in the curing of the impregnating compounds, after which oxidation begins and perhaps would continue until they were completely carbonized and the coils would have fallen to pieces. This point is less noticeable at 125° C. in the case of No. 2 gum and No. 35 gum. They have a higher melting point than No. 3 gum. However, at these temperatures they would never have lost their insulating qualities, but of course all mechanical qualities would have been gone and, consequently, the coils would become short-circuited.

The results show that continued heating is not particularly injurious to the electrical properties of these impregnating compounds, except insofar as they are dependent upon the mechanical qualities, which show considerable deterioration at 150° C., but little at the two lower temperatures.

In conclusion the writer wishes to state that this investigation was suggested, and the experimental part to a large extent carried out, by Dr. J. E. Shrader, formerly of this laboratory. He is, therefore, indebted to him for having the experimental data available.

DISCUSSION.*

W. G. Harvey[1]: I am interested to know the porosity of well-aged bakelite varnish. I have used it quite successfully for painting the outside of pipes intended for high vacuum use, and have been unable to decide whether several thin coats were better than one thick one.

H. C. P. Weber[2]: There are no visible pores. Bakelite itself is a very dense material, and very little gas will pass through it. In case the material is used in compositions, so-called micartas, or impregnated materials, the fiber structure dominates that system. In other words, if you have impregnated material you can get anything you want from complete water and moisture tightness to perfect penetrability. It is customary, of course, as determined

* In the absence of the author the above paper was presented by H. C. P. Weber

[1] Vice-President and Superintendent, American Magnesium Corp., Niagara Falls, New York.

[2] Research Lab., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

by the cost of the material, to stop at a reasonable impregnation. Actually, complete impregnation of the fibrous materials is really a difficult matter. If you have a micarta which does not have a large percentage of bakelite, the fiber will absorb moisture in spite of the bakelite which is there.

J. T. FitzSimmons[3]: During 1917 one manufacturer built quite a large quantity of apparatus for the War Department. A portion of it was bakelite or condensite, into which were molded metal and rubber inserts. This was a rather large piece and the curing process was long and the pressure rather high. This equipment has been used in service continually since that time. In that part of the equipment which has been in service and which must have of necessity undergone periodic heating and cooling, no trouble has been experienced, but another part of that equipment which has been in storage warehouses since 1917, or a year later, we occasionally find, upon putting it into service, that the bakelite or condensite seems to have deteriorated and we find the appearance somewhat changed. In other cases we find that an expansion apparently has taken place, and it has cracked around the metal inserts. Now whether that is due to a chemical process, I do not know. Apparently it is due to the presence of moisture, inasmuch as the humidity has been rather high, because the warehouses were unheated. With the apparatus which has been in continuous service, no trouble has been experienced.

Colin G. Fink[4]: What is the range of temperature in that warehouse?

J. T. FitzSimmons: I cannot give you that definitely. The warehouse was situated in Arkansas and was unheated. The humidity was probably high. We have made attempts to duplicate the conditions in the laboratory but, of course, the motors have been in the warehouses for quite a long period of time and duplication of the conditions is necessarily difficult.

Colin G. Fink: If the temperature range was, say, 20 or 30° C., that would be sufficient to account for the cracking of the bakelite around the metal inserts, because the expansion coefficient of the metal is four or five times that of the compound.

[3] General Motors Research Corp., Dayton, Ohio.
[4] Head, Div. of Electrochemistry, Columbia Univ., New York City.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE ELECTROCHEMISTRY OF GASES.[1]

By S. C. Lind.[2]

Abstract.

The present status of electrochemical action in gases is discussed and is compared with electrolysis. The necessity for indirect methods of investigation is mentioned and the gaseous reactions taking place under ionization by radioactive agencies are cited. Some new laws regarding ionization and chemical activation are stated which are supported by recent physical evidence and also chemically by the alpha ray kinetics of the decomposition of CO and of CO_2, the reduction of CO_2 by H_2 and the synthesis of CO_2 from CO and O_2 and of H_2O from H_2 and O_2.

In a previous paper[3] on "Gaseous Ions and Chemical Activity" before this Society, the writer advanced the view that ordinary electrochemical action and the Faraday equivalence represent a special case. All of the chemical action takes place at the electrode and the separation of the products may be regarded as a necessary consequence of the liquid-solid boundary existing there The general case of chemical action accompanying electrical conduction through gases is more complicated. Ionization and the reverse discharge by ionic recombination take place mainly in the bosom of the gas, not at the electrode. Such chemical action as may result has no direct relation to the current flowing and is usually greatly in excess of it, but does have a relation to the ionization. Since the quantity of ionization is unknown and can not even be estimated except under special conditions

[1] Published by permission of the Director, Bureau of Mines, Department of Interior, Washington, D. C. Manuscript received June 18, 1923.

[2] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.

[3] Trans. Am. Electrochem. Soc., **21**, 177-84 (1912).

of electrical discharge, indirect methods of investigation are necessary. An indirect method which the writer has found very useful consists in producing a known amount of ionization by means of radioactive agencies under conditions such that the chemical change produced is measurable. A statistical comparison of the number of reacting molecules "M" and the number of pairs of charges "N" indicates that the gas ions are chemically active and actually constitute the intermediate activated products of reaction. The results have an interest not only in connection with the electrochemistry of gases but also in the general subjects of chemical activation and catalysis, both positive and negative. Some recent discoveries in electronics support the assumptions made. Before discussing them, brief mention will be made of the results of others under actual electrical discharge in gases.

The investigation of chemical action accompanying electrical discharge through gases has taken two rather widely divergent courses, one of which has led to a study of "clean up" reactions at very low gas pressures where the main object is to get rid of all of the gaseous components. Great progress has been made in this field in the Research Laboratories of the General Electric Co. in this country and more recently in England. A fairly thorough comprehension of the relations has been obtained. Since the "clean up" usually takes place at the electrode, the case is really more like that of electrolysis. After the ions have been electrically neutralized, one is perhaps dealing with free atoms, and more progress has been made on that assumption. However, it is not fair to assume that the reactions in the second class of cases are likewise atomic rather than ionic. The second class embraces reactions carried out at normal or higher pressures under some form of electrical discharge. On account of the lack of information regarding either the amount of ionization or the nature of the individual ions under these conditions, development in this field has been slow and rather empirical. This is particularly unfortunate, since it is apparent that if we are ever to have an electrochemistry of gases, which shall occupy an important position in preparative chemistry, comparable to that of electrolytic chemistry, it will be in the region of relatively high, not of low, gas pressure discharge.

Since the reactions carried out under ionizing conditions produced by radioactive radiations are effective without limitations as to pressure, in fact more conveniently so at high than at very low pressures, the information gained from them is especially valuable provided the nature of the ions is the same as in electrical discharge. Here our information is rather meager. Millikan and his co-workers[4] have shown for several of the common gases that, when they are ionized either by alpha or beta particles, only one electron is removed from a single molecule. What happens to the positive rest ion is in doubt. It may dissociate into atoms or react without dissociating. Recent positive ray evidence of McHenry[5] indicates that in ionization by electronic collision, *molecular* ions are the predominant product; while in that by molecular ion collisions, *atomic* ions predominate as a result of a shattering effect. From this one might expect that the alpha particle would produce a complete shattering and that atomic ions and uncharged atoms would result. Such a conclusion, however, may be erroneous. The velocity of the alpha particle is of an entirely different order from that of the canal rays, and possibly an electron is "picked off clean" from the molecule without dissociating it, just as a high-speed projectile makes a clean hole in glass, while a slow one shatters it. At any rate the radioactive data of the writer are more in accord with the assumption of molecular ions as a result of ionization by alpha particles. The positive ray method appears incapable of telling us anything definite about the mass of ions at ordinary pressures, and one must depend on indirect evidence until a new method is devised; possibly spectral analysis will some time fill this gap.

To consider some of the indirect evidence supporting the assumption of ions as the actual intermediates of chemical reaction may be profitable.

Decomposition of CO. Calculations[6] from the early data of Cameron and Ramsay[7] indicated a ratio $\frac{M_{CO}}{N_{CO}} = 2$, meaning that

[4] Millikan and Fletcher, Phil. Mag. (6), 21, 753 (1911). Millikan, Gottschalk and Kelly, Phys. Rev. (2), 15, 157 (1920).
[5] J. J. McHenry, Phil. Mag. (6) 45, 433-43 (1923).
[6] Lind. J. Phys. Chem., 16, 589 (1912).
[7] Cameron and Ramsay, J. Chem. Soc. London, 93, 965 (1908).

two molecules of CO are decomposed for each molecule of CO that is ionized, M being the number of reacting molecules and N the number of pairs of charges. Recently this has been more accurately confirmed.[8] The reaction apparently is:

$$CO^+ + CO = \vdots\ (CO)_2^+ = CO_2 + (C)^+.$$

The electron liberated does nothing except to neutralize the final positive charge, which might be on the CO_2 as well as on the C, as far as we know at present; or, in fact, what occurs may be:

$$(CO)_2^+ + (-) = CO_2 + (C).$$

Two important facts are to be borne in mind for CO decomposition. First, the free electrons take no part in the chemical action through formation of negative ions and would not be expected to, since L. B. Loeb[9] has shown that CO, like H_2 and N_2, has very little affinity for electrons. The general law may be stated: *Free electrons will promote chemical reaction of gases only when a gas is present capable of forming a negative ion by attaching the free electrons.* When this is not the case they act merely to re-establish electrical neutrality.[10]

A second general law may be stated: *Gas ions tend to form charged complexes by attaching themselves to electrically neutral molecules. These complexes are the intermediate compounds of chemical reaction.* A physical support for this law may be seen in the work of Erikson[11] and of Wahlin[11a] in the "ageing" of ions where he finds that within a short period after formation, positive ions undergo a change in mobility indicating an increase in mass, which would be accounted for by such an attachment as indicated for CO^+. Besides illustrating a definite mode of intermediate compound formation by adding complexes, this reaction mechanism also appears to meet satisfactorily the objections that have been raised by Debierne[12] and Wourtzel[13] in the case of

[8] Results of Lind & Bardwell in forthcoming paper in the J. Am. Chem. Soc.
[9] L. B. Loeb, Phil. Mag. (6), **43**, 229-37 (1922).
[10] The Research Staff of the General Electric Co. of London, [Phil. Mag. (6) **42**, 244 (1921)] found the same M/N ratio of 2 by an electrical method and propose the same kind of general reaction mechanism except they assume no addition compound but a splitting when CO^+ and CO collide.
[11] H. A. Erikson, Phys. Rev. (2), **17**, 400 (1920); **20**, 117-27 (1922).
[11a] H. B. Wahlin, Phys. Rev. (2) **20**, 267-71 (1922).
[12] Debierne, Ann. de Physique (9), **2**, 97-127 (1914).
[13] Wourtzel, Le Radium **11**, 337 and 347 (1919).

M/N ratios considerably greater than 1. It not only makes higher ones plausible, but, as will be shown later, *necessary,* not only as high as 2, but even 4 and 6 in some cases.

In considering ions as types of *activated* molecules, some general conclusions may be drawn regarding activation since we know definitely just what the rate of ionization is. The third general law may be stated: *Activated molecules or atoms do not interact among themselves, but react with the unactivated molecules.* For example, the concentration of CO^+ ions would never be great enough for them to interact, but there is always an abundance of neutral CO molecules present. To extend this principle to photochemical and other forms of activation the recent observation of Weigert[14] may be cited, in which it was shown that the time of reaction of the photochemically activated Cl in the H_2-Cl_2 reaction is of the order 10^{-8} sec. Evidently the concentration of activated molecules or atoms would always be too low for interaction. The same kind of reasoning opens a way to the explanation of negative catalysis as recently pointed out by Taylor[15].

An atomic hypothesis of CO decomposition according to

$$CO^+ = C^+ + \vdots\, O + CO = CO_2,$$

would fit M/N = 2 equally as well as an ionic one. But the other splitting into O_2 and 2C, indicated both by the work of Cameron and Ramsay and of the writer, would fit only the complex $(CO)_2^+$ for reasons just brought out. In other words, O atoms at low concentration would combine with CO to form CO_2, not with each other to form O_2.

Carbon Dioxide. The case of the failure of CO_2 to be decomposed by alpha particles presents much interest. Wourtzel[16] has claimed that the CO_2 molecule is too stable. The writer[17] has expressed a doubt as to this explanation and wishes to propose the following one:

$$CO_2^+ + CO_2 = \vdots\,(CO_2)_2^+ + (—) = 2CO_2,$$

[14] Weigert, Sitzb. Preuss. Akad., 24, 315-20 (1922).
[15] H. S. Taylor, J. Phys. Chem., 27, 322-42 (1923).
[16] Wourtzel, Le Radium 11, 346 (1919).
[17] Lind, "Chemical Effects of Alpha Particles," 121 (1921).

obeying the same physical law as CO, but resulting in the same final as initial substance; hence producing no apparent reaction. This view seems to be confirmed by the following: H_2 was introduced as a possible "acceptor" in an effort to form a hydrogen complex with $(CO_2)^+$ and to cause it to be reduced. Experiments with 1-1 and 1-2 mixtures of CO_2 and H_2 showed rapid reduction at ordinary temperature by alpha particles. While the exact reaction and its products have not yet been definitely determined, the kinetics indicates $CO_2 + 2H_2$ as the stoichiometric reaction mixture. The intermediate complex would hence be $(H_2CO_2H_2)^+$ similar to $(H_2O_2H_2)^+$ in water formation, with the important difference that in the H_2 and CO_2 mixture free electrons play no part since neither H_2 nor CO_2 is a good electron trap. Kinetics also indicates in the H_2-CO_2 mixture that the encounters of CO_2 and CO_2^+ are ineffective and destroy the CO_2^+ without any reaction, just as if H_2 were not present. In short, we have the four possible partial reactions:

$CO_2^+ + 2H_2 = (H_2CO_2H_2)^+ \rightarrow$ Reduction of CO_2.

$H_2^+ + H_2 + CO_2 = (H_2CO_2H_2)^+ \rightarrow$ Reduction of CO_2.

$CO_2^+ + CO_2 = \vdots\ (CO_2)_2^+ + (-) = 2CO_2$ (No effective reaction).

$H_2^+ + H_2 = ?$.

It should be added that it has been proved kinetically that it is not a mere question of the formation of active hydrogen which reduces CO_2. The M/N ratio is also too great for such an assumption to be plausible.

The principle to be learned from the CO_2 reaction is that: *Ineffective encounters may destroy the activity of one of the components by leading to the reverse reaction.* This is shown by an M/N ratio < 1, which continues to decrease in a $1H_2$-$1CO_2$ mixture as the reaction mixture enriches relatively in CO_2 through the reaction $CO_2 + 2H_2$. This drop in velocity has been experimentally demonstrated, and is the controlling factor in spite of the increase in specific ionization in the mixture as the CO_2 is proportionately enriched.

The case of H_2O formation from $2H_2 + O_2$ under the influence

of Ra emanation has been treated by the writer[18]. The only change in the theory is necessitated by Loeb's[19] work showing that O_2 is a good electron trap while H_2 is not. Therefore, in the mixture $H_2 + O_2$ all the free electrons will be trapped by O_2 and none by H_2. This leads to an M/N ration of 4, as originally calculated, in agreement with experiments of the writer[20] and of Kirkby[21]. The intermediate complexes would be either $(H_2O_2H_2)^+$ or $(H_2O_2H_2)^-$ reached either from O_2^+, O_2^-, or H_2^+, *not from* H_2^-.

Oxidation of CO. Finally the case of $2CO + O_2$ presents great interest. The kinetics indicates that the reaction takes place according to the formula $2CO + O_2$. Since O_2 is present the electrons should produce active O_2^- as well as the positive rests O_2^+ and CO^+. The complexes will be therefore: $(COO_2CO)^+$ from either one O_2^+ or one CO^+ and $(COO_2CO)^-$ from one O_2^- but not from a CO^-. Therefore the ratio

$$\frac{M_{CO_2}}{N_{(CO + O_2)}} = 4 \text{ or, } \frac{M_{(CO + O_2)}}{N_{(CO + O_2)}} = 6,$$

which has been experimentally realized, and is in accord with the law enunciated. The combined reaction between CO andO_2 has also been shown to be faster than the reaction of the separate components CO and O_2, showing again that the electron is effective only when an electron trap like O_2 is present. In this the reaction is similar to the $H_2 + O_2$ reaction, with this important difference: in the reaction $2H_2 + O_2 = (2H_2O)$ the product H_2O is condensed and takes no further part in the reaction. In the case of $2CO + O_2 = 2CO_2$, the CO_2 accumulates in the system and is normally ionized by the alpha radiation. Since CO_2 is inert it would not be expected to take part in the reaction and the kinetics shows it to play no apparent role. This leaves in question why the free electrons from the CO_2 are not trapped by O_2, which one would expect to increase the reaction rate as CO_2 increases in partial pressure. The absence of such an effect

[18] J. Am. Chem. Soc., **41**, 558 (1919).
[19] L. B. Loeb, *loc. cit.*
[20] J. Am. Chem. Soc., **41**, 558 (1919).
[21] P. J. Kirkby, Phil. Mag. (6), **7**, 223 (1904); 9, 171 (1905); **13**, 289 (1907); Proc. Roy. Soc. **85A**, 151 (1911).

remains unexplained, unless an exact compensatory desactivation is caused by ineffective encounters, or else CO_2 retraps its own electrons before the O_2 molecule can receive them. The reduction of CO by H_2 has also been confirmed[22], but the reaction products have not yet been identified.

Conclusion. To return to the consideration of the present status of the general electrochemistry of gases, it is evident that we yet have far to go on the theoretical side. We lack exact knowledge of the amount of ionization and of the reactions of the ions under the most important conditions. Many complications arise which do not present themselves in electrolysis. We have but little indication that the field will ever be as fruitful as electrolysis has proved to be. The dearth of even accidental empirical discoveries would indicate that we must expand the scope of our efforts both in the theoretical and experimental directions. In the latter it would perhaps be well to pay more attention to extreme conditions both of discharge and of high gas pressure, as well as extreme conditions for rendering the products stable, such as low temperature or low temperature and adsorption combined. The great variety of ionic possibilities suggests a rich yield of new products or new synthetic methods for old ones, if we can learn to control the reactions, forcing them in desired directions and retaining the products initially formed.

SUMMARY.

As a result of kinetic studies of gas reactions under ionizing conditions (alpha radiation), the following new principles supported by recent electronic evidence may be stated:

1. Gas ions tend to form addition products with neutral molecules, which complexes are the intermediate products of gaseous electrochemical reactions.

2. As a deduction from (1) ions do not interact nor do molecules or atoms otherwise activated interact. Their momentary concentrations are too low. They react only with neutral or unactivated molecules.

[22] O. Scheuer, Comp. Rend. 158, 1887 (1914).

3. A low momentary concentration of activated substance is capable of explaining the action of negative catalysts or inhibitors.

4. Active ions may be destroyed by reverse action either in a uni- or multi-component system, without any effective chemical action resulting. This reversal may be prevented by a suitable acceptor.

5. Free electrons will play a primary part in producing chemical reaction only in gaseous systems containing at least one gas with affinity for electrons. Absence of such a gas will result in a reaction with a lower M/N ratio than when one is present. A secondary role is always played by electrons in restoring final electrical neutrality.

DISCUSSION.

FARRINGTON DANIELS[1]: (*Communicated*): Dr. Lind has clearly stated the present status of the electrochemistry of gases and blazed the way for further progress. The statement of laws is particularly valuable when so many isolated facts remain uncorrelated. The hypothesis of the formation of a complex as a first stage in chemical reaction receives support from many fields. Heterogeneous catalysis seems to demand the formation of a complex at the interface. Lowry has suggested that perhaps no true monomolecular reaction is known. Even the simplest of chemical reactions demands a catalyst, (water, for example). The decomposition of nitrogen pentoxide, a gaseous reaction which follows the calculation of a monomolecular reaction exactly, requires the presence of some nitrogen dioxide.

H. B. WAHLIN[2]: In the early work on gaseous conduction a lack of agreement was found between the theoretical calculations of the velocity of an ion through a gas and the observed value. In all cases the theoretical value was too high. This led to a cluster theory of ion formation; that is, the ions consist of clusters of molecules rather than single molecules.

Experiments have been carried out to disprove this theory by

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determining the mobility in high fields. In some experiments evidence was found for a breaking down of the cluster but the most recent work by L. B. Loeb shows that no such tendency exists.

Erikson, at Minnesota, has recently found that if the mobility is determined immediately after a cluster is formed, the value found is higher than if the ions are allowed to age for a short time (of the order of 1/100 sec.). This indicates a clustering. However, in this time the ions would make 10^7 or 10^8 impacts with the molecules. If there is a clustering then, we must assume that the ions select certain molecules to adhere to. This selection would probably depend on some surface condition.

On a small ion theory we would have to assume, in order to explain this ageing, that ionization consists not only in the removal of an electron but also in the splitting up of the molecules into atoms, with a subsequent recombination to form a molecular ion.

There is some evidence that this actually happens in the case of electron impacts, where the electron has a velocity corresponding to about 27 v. It is not safe to say, however, that the same thing would happen in the case of α-particle impacts where the energy is much greater.

Duncan MacRae[3]: In connection with Dr. Wahlin's discussion, I want to say a word of welcome to the physicists who have contributed so much valuable material to this symposium. I believe we electrochemists when taking up this subject seriously will find by referring to the physical literature that a solid foundation has already been laid upon which to build a new electrochemistry.

Louis Kahlenberg[4]: We are indebted to Dr. Lind for this summary. In Wiedemann's large treatise on "Elektrizität," conduction in gases is discussed, and attempts to determine the amount of chemical decomposition when the current passes through rarefied gases are mentioned. The amounts that must be measured are, of course, extremely small. Work on hydrochloric acid gas yielded the result that Faraday's law does not hold.

In our further studies of the problem of gaseous conduction

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[4] Professor of Chemistry, Univ. of Wisconsin, Madison, Wis.

we ought to be very careful to keep facts and theories separated. The facts we have are few, and we are viewing these in the light of a theory evolved from the study of aqueous electrolytic solutions.

Faraday made many experiments to get at the real nature of electrolytic conductions, yet he arrived at no conclusion as to why certain substances are electrolytes and others not. He found tin tetrachloride, a typical metallic salt, an insulator, and the bichloride of tin an electrolyte. These facts stand as unexplained today as ever. Again, why is silver such a good conductor, and sulfur an excellent insulator? We have some views on this matter, but no satisfactory explanation. I doubt much whether at this stage of the development of the subject we ought to take the view that conduction in gases is fundamentally different from conduction in solids and liquids. Faraday never considered ions as present except when the current was actually passing. The idea that ions are present before the current passes came from the study of dilute aqueous solutions that conduct, and this idea has been carried over to concentrated solutions and even to fused electrolytes. We now know of electrolytes whose vapor tensions differ very little from that of the pure solvent, yet they conduct well. Had such facts been known in 1887, it is doubtful if the electrolytic dissociation theory ever would have gained ground.

Further experimental work on the conductance of gases may well cast light on the real nature of electrical conductance and is, therefore, to be encouraged. Theories give suggestions that promote the work, but must not be permitted to lead us into a state of mental bias, if real progress is to result.

DUNCAN MACRAE: The electrochemical problems that Prof. Kahlenberg has mentioned, it seems to me, must ultimately find their solution in a study of the structure of the atoms. The relations between atoms and electrons are certainly of fundamental importance in electrochemistry, whether it be that of solids, liquids, or gases.

F. O. ANDEREGG[5]: Has Dr. Lind made any calculations of the number of collisions between his ions and unactivated molecules? The efficiencies are so high, that is, so close to the calculated

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values, that they suggest a life of the ions longer than he thinks, and that there are, relatively, a large number of collisions before reaction takes place. There is, therefore, a possibility that the molecule, which does not enter into reaction with the ions, must be activated, to a certain extent.

S. C. LIND: I have not attempted to go into the efficiency of the encounters. Evidently their number is very large. I think there is one possible way that it may be explained without assuming that the neutral molecule has received any activation from radiation, or any other source. That would be by taking count of the steric relation, whatever it may be, of the ion. These steric relations have been considered by some physicists; that is to say, an electron having been removed at one local point on the molecule, it may be that it must come into contact with the molecule with which it has to react, in just one particular orientation. If there is only small chance of its coming into that particular relation, you can explain an efficiency of one in a million, without necessarily assuming that anything has previously happened to the other (neutral) molecule.

CARL HERING[6] (*Communicated*): In dealing with the energy involved in those chemical combinations in which there is also a change of physical state, such as from a solid or liquid to a gas, or the reverse, there is an important physical energy involved which is quite distinct from the chemical energy, although usually this distinction is overlooked by combining the two together, as is done in stating the so-called heats of combination.

Thus when solid C combines with gaseous O the result is gaseous CO or CO_2; hence in this reaction the physical energies, that is the latent heats of liquefaction and of vaporization of the C, being endothermic, are deducted from the larger exothermic chemical energy of the combination. This is why the energy of $C + O = CO$ is so much less than that of $CO + O = CO_2$. From this difference the combined two latent heats of carbon can be calculated, if the chemical bond for each O is the same. On the other hand, when solid Mg combines with gaseous O forming the solid MgO, the latent heats of liquefaction and vaporization

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of O, being now exothermic, are added to the chemical energy. This may explain the intense light produced by this reaction.

A good reason for distinguishing between the physical and the chemical energies is that they follow different laws, and by recognizing this some processes might perhaps be improved or cheapened. The physical part for instance is dependent on the pressure, while the chemical part is not. The question has arisen, from where do the latent heats of vaporization of H and O come when liquid water is electrolyzed into gaseous H and O. If they come from the current it might be cheaper to do this under great pressure. If they come from the heat in the liquid (as when a liquefied gas expands under water) this energy costs nothing, being the free heat of the surrounding atmosphere.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

CHEMICAL ACTION AND THE DISAPPEARANCE OF GAS IN THE ELECTRICAL DISCHARGE TUBE.[1]

By F. H. Newman[2], D. Sc., A. R. C. S.

Abstract.

Hydrogen and nitrogen are absorbed in the presence of different elements, deposited on the cathode of a discharge tube, when the discharge is passing. The elements which show this effect most markedly are phosphorus, sulfur, iodine, sodium, potassium, and the alloy of sodium and potassium. The rate of disappearance is greatest with phosphorus, sulfur and iodine, and the final pressure attained is a minimum with phosphorus and sulfur. There is similar absorption when the gases are ionized by α-rays from polonium. The disappearance of the gas is due to the production of chemical compounds. The formation in this manner of the nitrides of sodium, potassium, magnesium and tin, and the hydrides of sodium, potassium and sulfur has been proved by chemical analysis. The gas under the ionizing effect becomes modified, assuming an active condition which consists probably of triatomic molecules.

INTRODUCTION.

The problem of the disappearance of a gas in the electric discharge tube is a very complicated one, owing to the many factors to be considered. The walls of the vessel and the electrodes will certainly receive some of the gas, although the latter may not disappear in its original state. There will be chemical changes occurring in the volume of the gas, such as the conver-

[1] Manuscript received June 8, 1923.

[2] Professor of Physics, University College, Exeter, England.

sion of carbon monoxide into carbon dioxide, and in addition, any other elements present in the discharge tube, either in the form of solid or vapor, will affect materially the rate of disappearance of the gas and the final pressure attained.

It is by no means certain that the same principles are at work in all these effects. It has been proved by chemical analysis, however, that in certain cases, such as when the liquid alloy of sodium and potassium is made the cathode in a discharge tube, and nitrogen is absorbed by it on the passage of an electrical discharge, definite chemical compounds—sodium and potassium nitrides—are formed.

When we come to consider the disappearance of nitrogen and hydrogen in large quantities in the presence of phosphorus in the discharge tube, the formation of any stable compound of phosphorus and nitrogen at first seems doubtful, and one is inclined to put forward a theory of occlusion or adhesion. In the present paper it is proposed to describe some of the actual results obtained when the discharge is passed through these gases in the presence of various elements, and in connection with these experiments to examine the conditions necessary for the absorption of the gas. Finally the theory of the phenomenon will be considered.

ABSORPTION OF NITROGEN.

Nitrogen is absorbed by most elements when an electric discharge is passed, particularly if the element is deposited in a thin film over the cathode, and the surface is quite clean and free from occluded gas. The absorption occurs in general only if the initial pressure of the gas is below 1 mm. of mercury, although sulfur, phosphorus and iodine are three striking exceptions, and in a lesser degree sodium, potassium and the alloy of these two metals.

The discharge will not eliminate all traces of the nitrogen, since at very low pressures gas is liberated from the element on the cathode by the bombardment with positive ions, but both forms of phosphorus "clean up" all the gas, and it is possible to reduce the pressure from any value to the vapor pressure of phosphorus. With sulfur the x-ray stage of pressure may be quickly attained.

In all cases the rate of absorption is greatest when the temperature of the discharge tube is maintained below 0° C., and in general, the lower the temperature, the lower is the final pressure reached. After the gas has been absorbed, part of it may be recovered by heating in the case of some elements, such as mercury, cadmium, antimony and zinc, but sulfur, iodine and phosphorus do not re-liberate any gas which they have absorbed.

The rate at which the gas disappears varies from one element to another, but is greatest with phosphorus. Including a water voltameter in the secondary circuit, the amount of gas disappearing in the tube has been compared with the amount of hydrogen liberated in the voltameter, and it was found that with few exceptions, more gas disappeared than hydrogen was liberated, particularly with the three non-metallic elements mentioned above. This proves that the absorption of the ions does not account for the large amount of gas which disappears.

ABSORPTION OF HYDROGEN.

With hydrogen, unless special precautions are taken, instead of getting the gas absorbed by elements, it is liberated, although phosphorus, iodine and sulfur are effective in disposing of the gas within the discharge tube even at high pressures. When the pressure is above 1 mm. of mercury a certain amount of gas within the tube becomes occluded in the walls. This gas will be re-liberated when the walls are bombarded by the ions produced in the electric discharge. This effect will mask any disappearance.

If, however, the tube is heated almost to the softening point of glass and highly exhausted, then on admitting hydrogen at a small pressure, such as 0.1 mm. of mercury, very little occlusion of the gas within the walls will occur, and on passing the electric discharge practically no hydrogen will be liberated by bombardment.

Most elements absorb hydrogen at pressures below 1 mm. of mercury, but it is not possible to eliminate all traces of the gas by the electric discharge. If the tube is heated after absorption has occurred, the amount of gas that can be recovered varies

considerably with different elements, but it is always less than that which has disappeared. This evolved gas is again absorbed when the discharge is passed, and is evidently hydrogen in the same condition as it was before disappearance.

There appears to be a fatigue effect whereby the actual amount of gas which can be absorbed by any surface is limited. This effect may be due to three causes. If the disappearance depends on chemical action the latter will occur mainly at the surface of the element. The formation of a chemical compound will thus protect the rest of the substance from the action, and the process will gradually cease. If on the other hand the effect is due to a deposition of the gaseous atoms on the surface, these atoms will diffuse slowly into the substance. The atoms arriving later will have less area on which to deposit themselves. A limit to the action will be reached when the number of atoms deposited is equal to the number set free by the bombardment of the surface by the ions.

The accelerating potential in the discharge tube affects, to some extent, the rate of disappearance of the gas, and also the final pressure attained. After absorption has occurred there will be liberation of the gas by the bombardment, and the final pressure reached must depend on the reverse action. The greater the accumulation of the gas on the surface of the cathode, the greater will be the amount of gas evolved.

When hydrogen is drawn from the discharge tube, and made to pass over a clean surface of the alloy of sodium and potassium, at first the surface is covered with a thin white crystalline compound when observed through a microscope. This white layer slowly changes on the admission of more gas to the dark grey colored deposit. This white crystalline film is a mixture of the hydrides of sodium and potassium.

Again, if the gas from the tube is led over sulfur, sulfuretted hydrogen is formed, as shown by the blackening of a paper soaked in lead acetate. These two experiments, together with the fact that nitrides are formed in the tube when sodium, potassium, magnesium and tin are present, show that the absorption is due in some cases to chemical action.

The disintegration of the cathode in a vacuum tube causes a film of metal to form on the adjacent glass. In this way a clean surface of metal is produced. When an electric discharge is passed the conditions are favorable for the absorption of gas by the metal.

The disappearance of nitrogen and hydrogen in the presence of the alloy of sodium and potassium has been utilized by the author in the construction of a vapor arc lamp. Two pools of the alloy form the electrodes within a quartz tube. When the lamp is tilted so that the two pools make contact, the arc is struck. This lamp will work with an applied potential difference of 40 v., and any gas present is absorbed by the electrodes under the action of the electric current. A good vacuum is thus maintained without recourse to continuous pumping.

EXPERIMENTS WITH α-RAYS.

It is to be expected that the effect of the rays from any radioactive substance, more particularly the α-rays, would be similar to the electric discharge at low pressure, for the radiations produce chemical effects in many substances. In some cases, such as the transformation of carbon dioxide into carbon, oxygen and carbon monoxide, complex molecules are dissociated, and in others complex molecules are built up, such as the formation of ozone from oxygen.

It has been found that when hydrogen is enclosed in a glass vessel coated with sulfur, iodine or phosphorus, and the gas is subject to the ionizing action of α-rays from polonium, the gas gradually disappears within the element present on the glass. This action only occurs at low temperatures in the neighborhood of —40° C. With nitrogen, other elements, including sodium, potassium, magnesium and the alloy of sodium and potassium, absorb the gas.

DISCUSSION.

The disappearance of gas in the discharge tube is due probably to several actions, some of which may be fundamental. It is

certain, however, that any attempt to explain the principles by the same theory would lead to conflicting results, but the processes occurring can be divided into two classes, chemical and mechanical. There is much evidence that the gas can be caused by the electric discharge to adhere to the solid parts of the discharge tube in some manner which is at present unknown. The gas is probably dissociated under the action of the discharge, and the atoms diffuse into the element. Heating the tube will cause these atoms to come off the surface and re-combine with other atoms to form molecules. One may question, however, whether this after all is not chemical action. No reason can be advanced for the non-reliberation of the whole of the gas which has disappeared.

The fact that when nitrogen is absorbed by phosphorus, sulfur and iodine, none of the gas is re-liberated, even when the tube is heated to the softening point, indicates the great stability of the chemical compounds formed. The nitrogen compounds appear to be more stable than those produced with hydrogen.

The chemical action may occur at the surface of the solid, or it may take place between the gas and the vapor of the element, but as the majority of the elements have very small vapor pressures it is unlikely that the action is due to the presence of the vapor. Under the influence of the electric discharge the gas assumes an active modification, and although this active condition is caused by the ions, results indicate that the number of active atoms or molecules in the gas is of a much higher order than the number of ions present in the gas at the instant of re-combination.

The law of constant proportion does not appear to be followed, but it must be remembered that there is always the reverse action —the liberation of gas by bombardment—and this effect may obscure the constant proportion law. It is of significance that the rate of disappearance of the gas increases, and the final pressure attained decreases, as the temperature of the vessel is lowered. This is due to increased activation of the gas as the temperature falls.

The formation of hydrogen sulfide by the action of active hydrogen on sulfur will not explain the disappearance of the gas, but it does indicate the production of a modified form of gas, which is able possibly to form other compounds with sulfur in addition to hydrogen sulfide.

The function of the ions produced by the α-rays does not appear to assist a chemical action between the gas and the element which otherwise does not occur, for the combination takes place after the ions have been removed. Probably the activity of the gas is due to an atomizing effect of the α-rays on the gas, the active product being monatomic gas. Some of the atoms will be formed at the surface of the element and will react chemically. Others will be produced in the volume of the gas, and will form triatomic molecules by collision with the neutral molecules.

The primary action of the α-rays appears to be the liberation of atoms of high activity. In addition, the rays produce δ-rays by their motion through gas, and these δ-rays may also be effective in producing the active modifications. The chemical actions occurring are probably determined by the heat necessary to effect the decomposition of the molecules, and not by the heat required for the final transformations and resulting products. That the α-rays produce active modifications of hydrogen and nitrogen, which in turn are able to react chemically with certain elements, strengthens the view that the disappearance of these gases in an electric discharge tube, in the presence of various elements, is also due to the formation of the active modifications of the gases by the electric discharge.

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DISCUSSION.*

S. C. LIND[1]: Mr. Newman's statement, top of page 83 of his paper, that "The function of the ions produced by the α-rays does not appear to assist a chemical action between gas and the element which otherwise does not occur, for the combination takes place after the ions have been removed," appears to be a misleading one.

By studying the details of Newman's work, which is referred to at the end of the paper, it appears that the primary reaction must have taken place in the polonium chamber, and that the activated hydrogen passed through the electrostatic field in an electrically neutral state. I think that Mr. Newman must realize this as he states in another part of his paper that probably the reactant is the active form of hydrogen, generally assumed to be H_3. I, therefore, do not believe that we should take Mr. Newman's statement too literally or assume that ions are not chemically active.

H. C. P. WEBER[2]: Whether this behavior is a physical or chemical combination appears to me as beside the question. Experiments which have been described in detail show that a mass of tungsten will hold one layer of oxygen more firmly than the regular oxide, whether it is a chemical compound or a physical compound. The combination lasts far beyond the temperature at which you can drive off tungsten oxide.

It is easy to confuse reactions between masses with reactions between individuals, and transfer conceptions from one to the other. That sulfur will not absorb or combine with oxygen (at ordinary temperatures) when present in mass, does not prove that one atom of sulfur will not "link up" with one atom of oxygen when they meet singly under the same conditions.

If we have the possibility of a molecule or an atom of phosphorus being thrown down on the wall simultaneously with a molecule of anything else along side of it, the residual affinities between the components may well be sufficient to knit the whole into a stable structure.

* In the absence of the author the above paper was presented by C. J. Thatcher.

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In the case of the phosphorus, that could, perhaps, be checked. You might speak, to avoid the word compound, of an alloy between phosphorus and hydrogen, of phosphorus and nitrogen. If you had a material of that kind on the wall of the tube or bulb the minute you got to a point where an allotropic change of the one kind of phosphorus to the other could be noted, then that gas retained should come off.

C. J. THATCHER[3]: It seems to me that the only importance of this question is that we might arrive at an understanding of the phenomenon, so that we could extend its use, if necessary. As to whether an absorption which is monomolecular or monatomic is physical or not, I would like to point out that the same effect occurs even with glass. You can shoot residual particles of gas into the glass walls of a vessel by ionizing them; and if you then heat the glass redhot, you can see the gas bubbles come out.

T. E. FOULKE[4]: In connection with "clean up" of residual gas in incandescent lamps, it is worth noting that an excellent summary of the subject is obtained in Mr. Dushman's book on "High Vacuum." One of the theories of "clean up" involves purely electrical phenomena. The gas is ionized by electron impact, and the ions thus formed are then driven into the walls by action of the electric field.

It is known that the introduction of phosphorus and like substances, increases the rate of "clean up." The phosphorus, aside from forming condensation nuclei for the positive ions, also deposits on the wall, covering the gas already cleaned up, and forms a fresh surface for further deposition of positive ions.

An experiment that has been made by several different experimenters, including the speaker, is the rate of "clean up" in weak, and strongly ionized, gases during the distillation of phosphorus from a filament to the bulb. It is found that the rate of "clean up" is slow if the gas pressure is less than one micron, and very rapid above two or three microns. In the first case there is weak ionization, and the phosphorus condenses on the wall so that most of the ions are driven on to the single surface. In the second, the phosphorus covers the positive ions as they are deposited.

[3] Chemical Engineer and Electrochemist, New York City.
[4] Belleville, N. J.

F. O. ANDEREGG[5]: Is glass a perfectly continuous substance or is it porous? If it is porous should this not be taken seriously into consideration?

COLIN G. FINK[6]: Dr. Anderegg's point is well taken. Recent experiments carried out on quartz glass show this to be comparatively porous.

LOUIS KAHLENBERG[7]: I note that iodine is mentioned in this paper as having an action similar to that of phosphorus. Some years ago I observed that when iodine is subjected to electrostatic strain in an ozonizer or similar contrivance, a white substance is formed. On removing the strain this white substance slowly changed back to iodine. The white substance proved to be an oxide of iodine.

COLIN G. FINK: The contention that nitrogen is cleaned up by phosphorus in a purely physical way does not always apply. Argon is a much heavier gas than nitrogen, and ought to be absorbed physically much better than nitrogen, but as a matter of fact it is not. We know of tungsten nitride and other nitrides, many of which are very unstable, but we know of no compounds of argon.

DUNCAN MACRAE[8]: Dr. L. Hamburger[9], has shown that a mixture of argon and nitrogen can be analyzed by passing the discharge through the mixture of argon and nitrogen (80 per cent argon and 20 per cent nitrogen) in the presence of white phosphorus vapor. As a result all the nitrogen will be removed from the mixture, leaving only the argon. That seems to be a quantitative method of determining nitrogen in the mixture.

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[6] Head, Div. of Electrochemistry, Columbia Univ., New York City.
[7] Professor of Chemistry, Univ. of Wisconsin, Madison, Wis.
[8] Westinghouse Lamp Co., Bloomfield, N. J.
[9] Proc. Acad. Sci., Amsterdam, 21, 1062-77 (1919).

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE DISAPPEARANCE OF GAS IN THE ELECTRIC DISCHARGE.[1]

By Research Staff, General Electric Co., Ltd.

Abstract.

Experiments were carried out with evacuated incandescent tungsten lamps and results indicate that the disappearance or "clean up" of the residual gases by phosphorus is due to the adhesion of the gas to a film of solid deposited by the discharge on the walls of the container. Other substances behave similarly to phosphorus. The inactive gases are more difficult to eliminate than gases such as oxygen or CO_2, and a possible explanation to account for this difference is suggested. [C. G. F.]

INTRODUCTION.

A complete summary of the more recent work of the "clean-up" of gases has recently been made by S. Dushman[2], and we do not propose to go over again the ground that he has covered so completely. Although the title of our paper is general, we propose to confine ourselves to the very small portion of the field with which our own experiments have been concerned. By way of describing that field we would point out that theories put forward to account for the facts may be grouped into two classes. The disappearance of gas has been attributed to chemical action, usually with the metal electrodes, which have been supposed to form with the disappearing gas some definite chemical compound which might be, even if it could not actually be, isolated and examined like any other chemical compound; or it has been regarded as "mechanical" and due to some absorption of the gas, usually on or in the glass walls of the vessel, its chemical condition being unchanged.

[1] Manuscript received June 16, 1923. Experiments recorded in this paper were carried out by the Research Staff of the General Electric Company, Ltd., Wembley, England, C. C. Paterson, Director.

[2] S. Dushman. General Electric Review. 24, 436-443, 669-680 (1921).

It is known now that, as usual, both theories are right. There are some "clean-ups" that are undoubtedly chemical. However, there are other "clean-ups" which are not clearly chemical; and they are perhaps more numerous than might appear at first sight, for some workers have apparently forgotten that a "clean-up" is not explained by a proof that chemical action occurs, unless the compound which is formed from the disappearing gas has a pressure at relevant temperatures much less than that of the gas. Among these "clean-ups," to which no chemical theory seems appropriate, is that by which traces of residual gas left in a highly exhausted vessel disappear when a discharge of any nature is passed, whatever the nature of the gas, the walls or the electrodes.

Intermediate between these extremes is a "clean-up" of the greatest practical importance. The disappearance of gas in the electric discharge is rendered much more rapid and complete if the gas is mixed with phosphorus vapor. This fact was discovered by Malignani[3] in 1894—although he did not describe his discovery in that way. Whitney[4] showed subsequently that arsenic, sulfur and iodine have properties similar to that of phosphorus in this matter. This process, which is involved in the manufacture of all electric incandescent vacuum lamps, resembles in some respects the "chemical" clean-ups, in others the "mechanical"; the part played by a substance of so great chemical activity as phosphorus suggests chemical action, while the similarity of the action in gases of every kind makes a chemical interpretation difficult. This is the action to which most of our attention has been directed.

IONIZATION AND THE "CLEAN-UP."

Some preliminary inquiries had to be made which require brief mention. If the disappearance of gas in the discharge is really due to the discharge, and if we are not being merely misled by secondary actions, there should be some intimate and simple relation between the rate of disappearance of the gas and the rate of ionization of its molecules; for a discharge is, in essence, nothing but a process of ionization. Working with a thermionic

[3] Malignani. Brit. Pat. 15129 (1894).
[4] W. R. Whitney. Trans. Am. Inst. Elec. Eng. 31, 921 (1921).

cathode and gases which should not exert any direct chemical action on this or the other electrodes, we were able to show[5] easily that no trace of a "clean-up" could be detected in any gas but hydrogen, unless the potential applied to the electrodes was sufficient to cause ionization of the gas; and further that the rate of disappearance increased generally with the ionization. Hydrogen was exceptional because, as Langmuir[6] has shown, it disappears by mere contact with hot tungsten.

In one special case a direct relation between ionization and disappearance could be established, namely when the gas through which discharge passed was carbon monoxide. The monoxide is converted into the dioxide, and the pressure decreases, partly because the number of molecules of the dioxide is less than that of the monoxide from which it is produced, partly because the dioxide is readily adsorbed on the walls. If part of the walls is cooled in liquid air and the dioxide removed continually, the disappearance of the monoxide and the formation of the dioxide will continue as long as the discharge lasts; but if the dioxide is allowed to accumulate the action is reversible.

It could be established[7] that the rate of reaction was proportional to the rate of ionization; that the reaction took place according to the scheme

$$2\ CO \rightarrow CO_2 + C$$

when a positive ion of carbon monoxide encountered a neutral molecule; and that, consequently, if an electrode could be arranged so as to receive all the charges on the positive ions formed and no other charges, then the relation between the current to that electrode and the mass of carbon monoxide undergoing the reaction would obey Faraday's electrolytic law, the constant of proportionality being that characteristic of an ion with valency ½. But it appeared also that the experimental conditions necessary for that law to be manifested were extremely difficult to obtain experimentally.

These results, we think, are interesting in themselves and important for any theory of chemical gas reactions. But their bear-

[5] Research Staff of the G. E. Co., Ltd. Phil. Mag. **40**, 585 (1920).
[6] I. Langmuit. J. Am. Chem. Soc. **37**, 1139 (1915).
[7] Phil. Mag. **42**, 237 (1921).

ing on our main inquiry is indirect. They show on the one hand that it is possible by electrical measurements to follow the processes concerned in a "clean-up," but, on the other, that even when the process is comparatively simple the relation between the current and the "clean-up" may be complicated in ordinary circumstances; the attempt to prove the occurrence of a chemical reaction by simply observing Faraday's law is likely to be misleading, unless the greatest care is taken to ensure that the current measured is really an indication of the rate of ionization.

THE "CLEAN-UP" WITH PHOSPHORUS.

We now turn to our main subject.[8] If a vessel is filled with the vapor of white phosphorus at any temperature below 250° C., and a discharge of any kind passed through it, the vapor disappears almost instantaneously and is deposited on the walls as a yellow or red film. The film does not disappear if oxygen is admitted and at room temperatures its vapor pressure is too low to be detected except by a sensitive ionization gauge. If the vessel is heated to any temperature below 250° C. the film is unchanged, but at 300° C. it disappears slowly in a vacuum and at 350° C. disappears in a minute or two. Meanwhile if a tube attached to the vessel is cooled, white phosphorus collects in it. Since the transformation from red to white phosphorus is known to start very slowly at about 270° C. these observations indicate that the discharge converts white phosphorus vapor into the red modification which is deposited on the walls. When we speak of "red" phosphorus, we do not mean to imply that the modification is exactly that of any particular form of solid phosphorus; for the differences between different colored modifications of this element are rather obscure; we mean only that the phosphorus is in the chemically inactive condition.

If the phosphorus vapor is mixed initially with gas of any other nature, the action of the discharge upon the phosphorus is unaltered; but some of the gas disappears at the same time as the phosphorus vapor. If the gas is hydrogen or nitrogen and the amount originally present is sufficiently small, the gas will disappear almost completely; the pressure will be reduced below that at which the discharge can continue to pass through the gas. If one of the

[8] Phil. Mag. 41, 685 (1921).

inactive gases is used, the disappearance will be less complete, but there will be a marked diminution of pressure. If now the vessel is heated as before, there will be no restoration of gas unless the temperature is sufficient to reconvert the red phosphorus into white; but as the red film disappears the gas originally present will be restored unaltered chemically and approximately in its original amount. Usually rather more gas appears than was introduced initially, but the excess can always be attributed to the evolution of gas from the walls either during the discharge or the subsequent heating. The temperature at which the gas reappears and the rate of reappearance at a given temperature is apparently quite independent of the nature of the gas that has been "cleaned up."

These observations would be difficult to reconcile with any chemical theory of the absorption by phosphorus. Such a theory would have to imagine a large number of chemical compounds with vanishingly small vapor pressures, which are quite unknown in other circumstances and of which all happen to decompose at the temperature at which red phosphorus is converted into white. It is much more likely that the disappearance of the gas is determined by the formation of the solid film of phosphorus on the walls, and that the gas which has disappeared is held to the walls by this solid film. At first sight—this view is probably too simple to account for all the facts—we may be inclined to think of the solid film as providing a gas-tight layer between which and the glass the gas is entrapped.

Support for the view that this form of "clean-up" is connected with the formation of a solid layer on the walls of the vessel is obtained when it is noted that the formation of other solid layers may also be attended by the disappearance of gas. Thus it has long been known that the "clean-up" in the discharge is closely associated with the sputtering of the cathode; in early days of x-ray work it was recognized that a bulb would always run hard when it blackened; the connection between sputtering and "clean-up" as investigated in some detail by Brodetsky and Hodgson,[9] and Vegard's experiments[10] which showed that the rate of "clean-up" was largely determined by the cathode fall (which is known to determine sputtering) emphasized the connection.

[9] S. Brodetsky and B. Hodgson. Phil. Mag. **31**, 478 (1916).
[10] L. Vegard. Ann. d. Physik. **50**, 769 (1916).

Again Langmuir[11] has shown that the production of a solid film of tungsten and other metals on the walls of a glass vessel causes a rapid and complete "clean-up," even when the film is formed by thermal evaporation unaccompanied by any discharge. We have shown that other solid films are equally effective. If the tungsten filament of an incandescent lamp is coated with various salts, such as the alkaline fluorides and chlorides, sodium silicate, silica or powdered glass, then if the filament is heated to 2,000° C. or more (at which temperature all these salts evaporate in a vacuum) the transference of the salt from the filament to the walls is accompanied by a "clean-up" of any gas which may be present, closely similar to that which accompanies the evaporation and deposition of phosphorus. The powdered glass may be of precisely the same nature as that of which the vessel is composed; the material of the walls is not altered by the disposition, unless possibly there is chemical alteration of the glass during evaporation.

QUANTITATIVE MEASUREMENTS.

Though the "clean-up" is particularly rapid during the deposition on the walls of these films of phosphorus or other materials, it may still continue, if the discharge is continued, after the deposition is complete. But since in these circumstances there would be some "clean-up," even if the film had not been deposited, and if the walls were in their natural state, quantitative measurements are necessary to determine the effect of the film. We have made such measurements, using as discharge vessels ordinary tungsten incandescent filament lamps. In such lamps, especially when designed for higher voltages (200 or more), there is a discharge between the negative end of the filament, which acts as a thermionic cathode, and the positive end which acts as anode.

In the fully evacuated lamp, used in practice, the current flowing in this discharge is purely electronic and limited by the space charge around the cathode; it amounts only to a few microamperes. But if gas is present and the space charge neutralized, a current of several milliamperes may flow. Such lamps are peculiarly well suited as discharge vessels for this kind of work, because the metal parts are so small that any effects they may have

[11] I. Langmuir. Z. Elektrochem. 15, 516 (1914).

on the "clean-up" are negligible, and also because they can be obtained in unlimited numbers and a fresh vessel used for each experiment.

For the methods of determining the decrease in pressure due to the "clean-up" reference must be made to our original account.[12] It will here suffice to say that in most of the measurements a determination was made of the greatest amount of gas that could be cleaned up so completely that a high vacuum was produced and the current limited by the space charge.

It appeared from preliminary observations that the amount of gas that could be cleaned up by a given amount of phosphorus was independent, within wide limits, of the initial pressure of the gas. On the other hand, as might be expected, it varied somewhat with the shape of the vessel, which determines the area on which the film is deposited. The total amount of gas cleaned up was independent within wide limits of the current passing through the discharge (this current could be varied by varying the temperature of the filament), but the proportion of the total "clean-up" which occurred in the first stage, during the deposition of the film, to that which occurred in the second and slower stage, after that deposition, varied considerably with the nature of the discharge. At first only the total amount cleaned up in the two stages was measured.

The results obtained are indicated by the full line in Fig. 1, which gives the relation between the mass of the hydrogen cleaned up and that of the phosphorus introduced. The experiments are difficult and some of the points are liable to considerable error. But the features which seem to us of particular importance are clear: first, when the amount of phosphorus is small, the "clean-up" increases rapidly with that amount; second, that a stage is then reached when addition of phosphorus causes no further increase in the "clean-up"; third, that the "clean-up" increases again, but much more slowly, when the phosphorus is increased beyond this point. Precisely similar results were obtained with nitrogen; indeed if the volumes (and not the masses) of the two gases were compared, the volumes cleaned up by the same amount of phosphorus seemed the same for the two gases.

In these experiments the phosphorus was coated on the fila-

[12] Research Staff of the G. E. Co., Ltd. Phil. Mag. 43, 914 (1922).

ment, so that it was evaporated immediately the filament was heated and the discharge started. But since it had been found that the "clean-up" was continued even after the deposition of the film was complete, it was interesting to inquire what would hap-

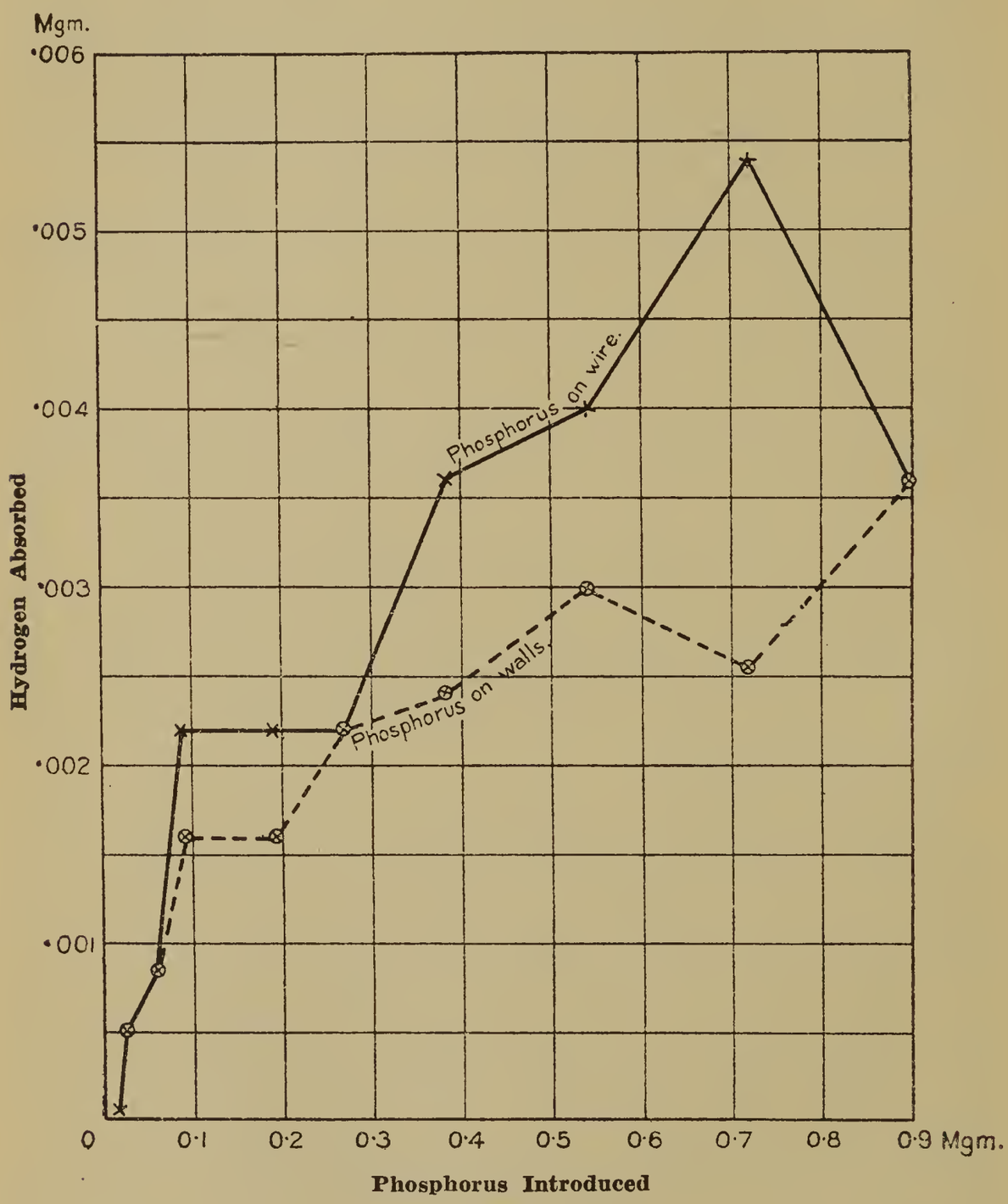

Fig. 1

pen if the film were deposited before any gas were introduced. The observations made in these circumstances are shown by the dotted line, which is generally similar to the complete line; the "clean-up" is generally less.

Measurements made with salts, such as sodium fluoride and silicate, in substitution for phosphorus were less complete; but the same general relation was found. There was the same rapid rise for small amounts of the salt, followed by a region in which the "clean-up" was independent of the amount of salt. Further, the amount of gas cleaned up when this stage was reached was, at least approximately, the same for all salts and for phosphorus.

It is natural to identify this stage with that at which the phosphorus or salt introduced is just sufficient to form a complete layer on the walls of the vessel; estimation of the amounts to form a monomolecular layer are not inconsistent with this hypothesis; the observed are certainly greater than the calculated amounts, but on the other hand it is by no means certain, or even probable, that the layer deposited is of uniform thickness.

THE LIMITING PRESSURE.

The result of all these observations was to indicate that there is nothing specific in the action of phosphorus, or of the other elements, arsenic, sulfur and iodine, which behave in the same manner. Its action in producing a "clean-up" was simply due to the formation of a film on the walls under the action of the discharge. There is one respect, of great importance in practical applications, in which phosphorus and the associated elements differ from the salts and from all other materials that we have investigated. If phosphorus is used and the gas initially present is insufficient in amount to exhaust the whole amount of phosphorus introduced, the "clean-up" will continue indefinitely; as the pressure is reduced the rate of "clean-up" falls off rapidly, but we have never been able to obtain evidence that it ceases; by means of the phosphorus "clean-up" with a discharge from a thermionic cathode vacua can be obtained as high as by any other method; the practical limits of a sensitive ionization gauge can be reached. On the other hand when salts are substituted for phosphorus, the pressure never falls below a certain limit, even if the total amount of gas cleaned up is much less than the greatest with which the salt can deal at higher pressures.

In the final stages the "clean-up" seems to become reversible

and the absorption of gas to be balanced by evolution. This is what might be expected, for it is known that if there is gas deposited on the walls of a discharge vessel, such as the adsorbed layer which normally adheres to solids that have been exposed to the atmosphere, the passage of a discharge through the vessel will liberate it. In order to explain the limiting pressure, it is only necessary to assume that the cleaned up gas, though adhering more firmly than the adsorbed gas, is still capable of being removed by bombardment.

Then why is the "clean-up" with phosphorus, and also arsenic, complete? We believe that the reason is to be found in the fact that phosphorus, unlike the salts, is itself detached by bombardment, reconverted into the gaseous state and once more deposited. Of such reliberation of the phosphorus definite proof can be obtained; for, if more gas is added than the phosphorus will "clean-up" and the discharge continued, the phosphorus will gradually accumulate in the parts of the vessel through which the discharge does not pass. Just exactly why this continual liberation and redeposition of phosphorus enables a complete "clean-up" of the gas to be attained finally, we do not profess to understand; more must first be known of the method by which the cleaned-up gas is attached to the walls.

We have made a few experiments of the rate at which the "clean-up" occurs in the hope of obtaining such information. But our results are at present incomplete. The observations are extremely difficult, because so many factors enter, of the exact nature of which we are yet unaware. All that we have established is that, during the latter stages of the "clean-up" by phosphorus, when the film has been completely deposited on the glass, a condition can be obtained when, within wide but finite limits, the rate of disappearance of the gas varies as the square of the ionization. On the other hand, when the film consists of a salt, the rate of disappearance appears to vary more nearly directly as the ionization. The second relation would obtain if a certain proportion of the atoms ionized adhered to the film, the first if a certain proportion adhered to the film, while another proportion put the film in a fit condition to receive them, possibly by the

liberation and deposition of new material. But such suggestions are highly speculative.

CONCLUSIONS.

To sum up, what our experiments appear to prove is that the "clean-up" by phosphorus is due to the adhesion of the gas in some manner at present unknown to a film of solid deposited by the discharge. The action is not peculiar to phosphorus, but is imitated by many other substances, which can similarly be deposited as films on the walls. What is the nature of the adhesion is at present unknown; but provisionally we may perhaps imagine that the deposited film is electrically polar, having a charge of determinate sign directed towards the interior of the vessel. Ions arriving at the walls with charges of opposite sign would adhere to such a film.

The greater difficulty of cleaning up the inactive gases (it must be remembered that they can be cleaned up to some small extent, especially during the stage when the film is being deposited) would then be due to the greater difficulty of charging their atoms. Indeed, if it is the negative rather than the positive ions which adhere, the difficulty of forming negative ions of these gases might account for their exceptional behavior. And if such a film can be formed to some extent even on the surface of glass, and other materials, in their "natural" condition, the "clean-up" of a pure gas under the action of the discharge, without the addition of phosphorus or of any of its substitutes, might be brought into line with the actions that we have studied more specifically.

On this view the "clean-up" of gases by the discharge would be another illustration of the remarkable properties of surface films, which have been studied so fully by Langmuir and by those who have followed him. If chemical combination is a manifestation of electrostatic forces, exerted not necessarily between charges separated into distinct atoms, then the adsorption with which we have been concerned is in some sense chemical; it is probably as chemical as the formation of oil films, which can be directly related to the chemical properties of the oil molecules. But it is not chemical in the sense that it results in the formation of definite chemical compounds, characterized by constant propor-

tions, which can be separated bodily from the medium in which they are formed.

DISCUSSION.*

C. J. THATCHER[1]: As I view this "clean-up" phenomenon, at least in the case of phosphorus, there is no proof of the occurrence of a chemical combination. Take for example, an incandescent lamp with some red phosphorus "getter" deposited in the tubulature. After the air is pumped down to 1 mm. and comparatively few gas molecules remain, heating the tube with a blow torch changes the phosphorus into vapor which spreads into all parts of the lamp. Then, when the filament is intensively incandesced, ionization results, and causes precipitation of innumerable dust-like particles of phosphorus, in a manner much like precipitation by the Cottrell process.

The surface of these particles is something like a million times as great as the phosphorus deposit from which they came; and at the moment of precipitation all of that surface is necessarily free from gas film. Consequently the few remaining gas molecules in the bulb are deposited on the gas-free surfaces of the solid phosphorus particles, as a result of that physical attraction whereby, as we know, every solid is covered by a film of gas; near the surface of the solid at least, the film of gas approaches the density of a solid. I think this is the rational and proven explanation of this "clean-up" phenomenon.

Mr. Newman believes that a chemical compound is formed, because hydrogen is absorbed when it is passed over an alloy of sodium and potassium, giving a white crystalline film visible under a microscope. He does not state at what pressure that occurs. Unless it occurs at low pressures such as 1 mm. or less, it does not prove that you get a chemical compound in a "clean-up." For even white phosphorus, which we all know readily unites chemically with oxygen under normal conditions, does not absorb oxygen at low pressures such as we have in incandescent lamp exhaustion. In the absence of ionization it takes about 45 min. I think,

* In the absence of the author the above paper was presented by C. J. Thatcher.

[1] Chemical Engineer and Electrochemist, New York City.

to absorb oxygen at 1 mm. pressure from an incandescent lamp with white phosphorus.

The "clean-up" we are talking about is instantaneous. What occurs at higher pressures does not prove chemical combinations at the very low pressures of incandescent lamp exhaustion, either with phosphorus and oxygen or with hydrogen and sodium. I doubt if nitrogen instantly unites chemically with phosphorus, at any such low pressures as we have in incandescent lamp exhaustion.

C. G. SCHLUEDERBERG[2]: What becomes of that film of phosphorus—all of those particles deposited on the walls?

C. J. THATCHER: I have never been able to find such a film even under the microscope. The amounts of phosphorus and gas we are talking about are infinitely small. I have seen oily finger print markings on the inside of broken incandescent lamp bulbs which can be, and have been, mistaken for particles of phosphorus oxides.

F. A. LIDBURY[3]: In the case of the "clean-up" by phosphorus, I think a great deal of the apparent mystery will disappear if we cease to confuse, in this discussion, the white and amorphous modification. The paper speaks of amorphous phosphorus as covering a number of different colored modifications of the element, the connection between which, it states, is somewhat obscure. I do not believe that this obscurity requires any further clearing up than the assumption that the different varieties exist in what our colloid friends would call different degrees of dispersity. At all events, amorphous phosphorus is characterized by a high degree of surface development, and consequently a high adsorptive power. For versatility of properties among the elements it has no rival, unless it be amorphous carbon. Its adsorptive qualities, in fact, are such that the literature is full of descriptions of phosphorus compounds which, except in the sense in which Dr. Langmuir regards adsorption as a chemical effect, are not chemical compounds at all.

In the "clean-up" the bulb is first filled with phosphorus vapor, or, insofar as this condenses, droplets of white phosphorus. In

[2] Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[3] Works Manager, Oldbury Electrochemical Co., Niagara Falls, N. Y.

this condition it has no "clean-up" power. Presumably this is given to it by the flash, which converts the vapor into the amorphous modification of the element in a very finely divided state and possessing high adsorptive powers; and the particles (of amorphous, not white phosphorus) will pick up those gases at any rate for which they have a specific high adsorptive capacity, and, whether by electrostatic precipitation or otherwise, the particles with the gases are removed from further participation in what goes on in the lamp, unless the lamp is again heated to a temperature at which the amorphous phosphorus formed is again vaporized, when of course the gas is again liberated.

You will note that this is consistent with the curve given on page 94, which, all things considered, comes pretty close to the familiar thing which is known in colloid chemistry as an adsorption isotherm; the surprising thing being not that the agreement is not closer, but that it is as close as it is, in view of the fact that the degree of dispersity of the amorphous phosphorus particles formed must vary considerably, owing to differences in the conditions of their formation, which need only be slight to have a considerable effect.

S. C. Lind[4]: In the matter of the foregoing discussion on the paper by Mr. F. H. Newman as to whether we are to assume that the "clean up" reaction is of chemical or physical nature, I believe we are practically agreed fundamentally. This paper of the Research Staff lays stress on the successive formation of new solid layers through the deposition of phosphorus or other substances. The continual formation of a new layer presents the opportunity for further reaction. If one then is dealing with monomolecular phenomena, whether one wishes to regard that action as physical or chemical appears to be a matter of choice.

Langmuir has shown that the monomolecular reactions on surfaces is on the border line between physical and chemical action, and one should not forget that matter in the monomolecular state does not have the ordinary properties of matter in mass.

[4] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Colin G. Fink in the Chair.

THEORY OF ELECTRON EMISSION.[1]

By Saul Dushman.[2]

Abstarct.

In this paper the Nernst heat theorem is applied to the evaporation of electrons. The theoretical treatment is analogous to that already developed for the evaporation of a monatomic substance. This leads to an equation for the electron emission from metals as a function of the temperature, which is different from the classical form derived by Richardson. Experimental data on the emission from various metals are found to be in satisfactory agreement with this new equation. The paper also discusses the problem of efficiency of electron emission, and the effect of field strength on emission.

DERIVATION OF RELATION FOR ELECTRON EMISSION.

On the basis of the electron theory of metallic conduction O. W. Richardson [3,4] derived a relation for the electron emission from metals as a function of the temperature, which is of the form

$$I = A_1 \sqrt{T}\, \epsilon^{-b/T} \qquad (1)$$

In this equation A_1 is a constant whose value is proportional to the number of free electrons per unit volume, while b is proportional to L, the latent heat of evaporation per mol of electrons, according to the relation

$$b = L/R \qquad (2)$$

where R = 1.987 cal. per deg.

[1] Manuscript received June 20, 1923.

[2] Research Lab., General Electric Co., Schenectady, N. Y.

[3] O. W. Richardson, The Emission of Electricity from Hot Bodies. Longmans, Green and Co., 1921; O. W. Richardson, Trans. Am. Electrochem. Soc. 21, 69 (1912).

[4] I. Langmuir, Trans. Am. Electrochem. Soc. 29, 125 (1916).

From this theory it follows that A_1 and b are specific constants for each metal or electron emitting surface.

Although equation (1) was found to be in excellent agreement with the experimentally observed data on electron emission there has been a certain amount of dissatisfaction with the theoretical arguments, on which it is based. In fact, Richardson himself suggested, in 1914, a modified form of equation (1) which is formally similar to that derived recently by the writer, but apparently this suggestion was not considered sufficiently important for further investigation.

A new method of approaching the problem of electron emission was suggested by the publications of Megh Nad Saha[5] and R. C. Tolman.[6]

The former applied the Nernst heat theorem to calculate the degree of ionization of metallic vapors at very high temperatures, while the latter showed that it is possible to treat the problem of electron emission in a similar manner, as thermodynamically analogous to the evaporation of a monatomic gas.

Stated very briefly, the Nernst heat theorem gives a relation between the available or free energy of a reaction and the change in total energy. Now in the case of evaporation the work available can be calculated from vapor pressure data. On the other hand the change in total energy corresponds to the heat of evaporation. As well known, the latter may be calculated from the temperature coefficient of the vapor pressure by means of the equation

$$\frac{d\ln P}{dT} = \frac{L}{RT^2} \tag{3a}$$

Assuming that L is practically constant this equation may also be written in the form

$$\frac{d\ln P}{d(1/T)} = -\frac{L}{R} \tag{3b}$$

or

$$\frac{d \log P}{d(1/T)} = -\frac{L}{2.303\ R} \tag{3c}$$

[5] Megh Nad Saha, Phil. Mag., **40**, 472 (1920).
[6] R. C. Tolman, J. Am. Chem. Soc. **43**, 1592 (1921).

That is, if we plot log P against 1/T, the slope of the straight line thus obtained is a measure of the latent heat of evaporation. The integration of this differential equation leads to the result

$$\log_{10} P = -\frac{L}{2.303\ RT} + C \qquad (3d)$$

where C is an integration constant.

It is evidently impossible, without a knowledge of C, to calculate P at any temperature from observed values of L, or vice versa to derive L from any individual value of P. The Nernst heat theorem, however, enables us to accomplish this object inasmuch as it indicates the manner in which equation (3) may be integrated, even for those cases in which L varies with T.

Now what Tolman pointed out is this: that if we consider the emission of electrons as analogous to the evaporation of a monatomic gas (of very low molecular weight to be sure, since $M = 5.44 \times 10^{-4}$ g.) we can make use of the Nernst heat theorem to calculate the heat of evaporation from the observed emission data at any temperature. On the other hand, the heat of evaporation may be calculated either from the actually observed value of cooling effect due to electron emission, or from the observed temperature-coefficient of electron emission by means of equation (3). Tolman finds that in the case of tungsten, molybdenum and tantalum, for which the electron emission data are most reliable, the values of the heat of evaporation calculated by applying the Nernst theorem agree very satisfactorily with those observed experimentally.

In order to apply equation (3) to the case of electron emission, it is obviously necessary to calculate the vapor pressures of the electrons from the emission data. The principle on which this calculation is based was first pointed out by Knudsen[7] and has been applied very extensively by Langmuir[8] to calculate vapor pressures from rates of evaporation. According to the kinetic theory of gases, the rate at which molecules strike a surface is given by the equation

[7] M. Knudsen, Ann. Physik 28, 75; 28, 999 (1908); also see S. Dushman, Production and Measurement of High Vacuum, General Electric Review, 1922.

[8] I. Langmuit, Phys. Rev. 2, 329 (1913), and subsequent papers.

$$n = \frac{6.062 \times 10^{23}\ P}{\sqrt{2\pi\ MRT}} \tag{4}$$

where n = number of mols per cm.^{2} per sec.

In the case of a solid in equilibrium with its vapor, the number of molecules striking the surface must be equal to the number leaving the surface. Assuming that there is no specular reflection of molecules at the surface, it is evident that equation (4) also gives the rate at which molecules evaporate from the surface.

If, now, we apply equation (4) to the evaporation of electrons, the rate of emission of electrons is given by I/F where I = emission in amp./cm^2 and F = 96,500 coulombs.

Hence

$$\frac{I}{F} = n \tag{5}$$

Equation (3) may therefore be written in the form

$$\frac{d\ln\ (\sqrt{T})}{dT} = \frac{L}{RT^2} \tag{6}$$

where L corresponds to the heat of evaporation per mol of electron.

It is evident, on the basis of Tolman's results, that there must exist a relation between I and L which resembles that between p and L. In other words, we should be able to determine the constant in the integration of equation (6), and furthermore, it is evident that this constant must be related to the constant of integration in equation (3d).

The latter is usually known as the "chemical constant" and on the basis of certain theoretical considerations O. Sackur[9] and Tetrode[10] showed that for any monatomic gas this constant has the form

$$C = C_0 + \frac{3}{2} \log_e M$$

where M = molecular weight, and C_0 is a function of the constants R, h (Planck's quantum constant) and N (Avogadro's constant).

[9] O. Sackur, Ann. Physik, 36, 598 (1911); 40, 67 (1913).

[10] H. Tetrode, Ann. Physik, 38, 434; 39, 255 (1912), also see G. N. Lewis and M. Randall, Thermodynamics, McGraw-Hill Book Co., 1923.

More recently Lewis, Latimer and Gibson[11] have used the theory of rational units to derive a slightly different value of C_0. From experimental data on vapor pressures and specific heats it is not possible at present to decide definitely in favor of either theory, although that suggested by Lewis and his associates appears to be the more logical.

Applying these considerations it has been shown by the writer[12] that the equation for electron emission assumes the form,

$$I = A_0 T^2 \epsilon^{-b_0/T} \tag{7}$$

where A_0 is an integration constant whose value may be calculated from that of C_0 and M for electrons, and $b_0 = L_0/R$. In this case L_0 denotes the heat of evaporation at the absolute zero.

On the basis of the Sackur-Tetrode theory, it is found that $A_0 = 60.2$ amp./cm.^{2} deg.^{2} while the theory of Lewis leads to the value $A_0 = 50.2$. In either case this constant *has the same value for all substances.* Thus the significance of equation (7) is that it involves *only one unknown constant,* b_0, instead of two as in Richardson's equation. Different electron emittors vary only in regard to the value of L_0, the heat of evaporation of the electrons. Furthermore, it is evident that in order to determine b_0 it is only necessary according to equation (7) to measure the electron emission I at any given value of T.

It might appear at first glance a very simple matter to decide from emission data between the two values of A_0. Since, however, T occurs in the exponent it is evident that even a slight error in the determination of the temperature leads to a much greater error in that of A_0. The experimental data obtained in our laboratory in conjunction with the temperature scale for pure tungsten as derived by Worthing and Forsythe[13] are in somewhat better agreement with the value $A_0 = 60.2$; so that provisionally we have used this value in the application of equation (7). But this must not be considered as a test of either the Sackur-Tetrode or the Lewis theory.

[11] G. N. Lewis, G. E. Gibson and W. M. Latimer, J. Am. Chem. Soc. 44, 1008 (1922).

[12] S. Dushman, Phys. Rev. 20, 109 (1922); 21, 623 (1923).

[13] A. G. Worthing and W. E. Forsythe, Phys. Rev. 18, 144 (1921).

The validity of equation (7) which we shall now write in the forms

$$I = 60.2\ T^2 \epsilon^{-b_0/T}\ \text{amp./cm.}^2 \qquad (7b)$$

or

$$\log I = 1.7792 + 2 \log T - \frac{b_0}{2.303\ T} \qquad (7c)$$

has been tested by the writer and his associates for a number of metals over a large range of temperatures.[14] In all cases the emission data have been found to be in agreement with this equation, within the experimental limits of error in the determination of temperature.

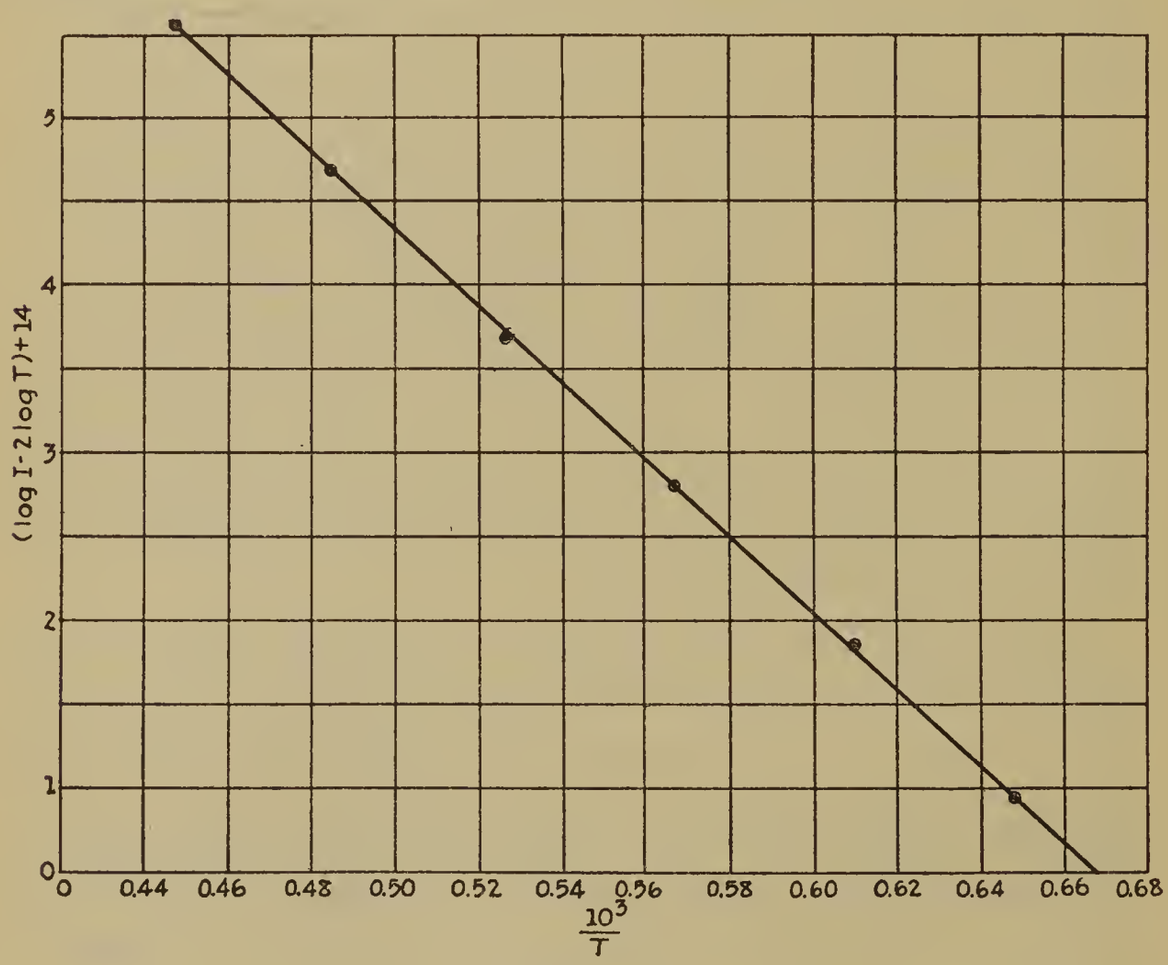

FIG. 1

Plot of log (I/T^2) against $1/T$. Data given in Table I. Slope of line corresponds to $b_0 = 52{,}700$.

As an illustration of the general character of the data obtained, Table I is given, showing results obtained with a filament of pure tungsten.

[14] S. Dushman, H. N. Rowe and C. A. Kidner, Phys. Rev. **21**, 207 (1923). The complete paper will appear in the near future.

TABLE I.

Electron Emission From Pure Tungsten.

T	Log I	Log (I/T^2)	$10^3/T$	b_0
1470	$\bar{8}.5272$	$\overline{14}.1926$	0.6803	52,770
1543	$\bar{7}.3280$	$\overline{14}.9514$	0.6482	52,700
1640	$\bar{6}.2672$	$\overline{13}.8376$	0.6098	52,650
1761	$\bar{5}.2986$	$\overline{12}.8072$	0.5679	52,600
1897	$\bar{4}.2655$	$\overline{11}.7093$	0.5271	52,720
2065	$\bar{3}.3031$	$\overline{10}.6731$	0.4842	52,840
2239	$\bar{2}.2659$	$\overline{9}.5659$	0.4467	52,640
				Av. = 52,700

It will be observed that while the emission varies over a range of 500,000 : 1, the values of b_0 corresponding to each individual determination of the emission show practically no variation.

Furthermore, if log (I/T^2) is plotted against $1/T$, it follows from equation (7c) that the points should lie on a straight line whose slope is $b_0/2.303$. Fig 1 shows the plot of the emission data in Table I, and the slope of the straight line is actually found to correspond to the value $b_0 = 52{,}700$.

Similar results, all in satisfactory accord with equation (7) have been obtained not only for different samples of tungsten wire, but also for other metals.

RELATIVE EMISSION FROM VARIOUS SUBSTANCES.

As mentioned previously, it follows from the equation presented in this paper that various substances differ in emission only because of differences in the value of b_0. Fig. 2 shows a series of graphs of equation (7c) in which log I is plotted as ordinate against b_0 at constant value of T.[15] For two substances at the same value of T,

$$\log I' - \log I'' = \frac{b_0'' - b_0'}{2.303\ T} \qquad (8)$$

where I', b_0' and I'', b_0'' refer to each substance respectively. Thus,

[15] S. Dushman and Jessie W. Ewald, General Electric Review, 26, 154 (1923). Fig. 2 is taken from this paper which gives data on the emission and efficiency of emission from tungsten, thoriated tungsten, molybdenum and tantalum.

for tungsten, $b_0'' = 5{,}600$, while for thoriated tungsten, $b_0' = 34{,}100$. Hence, at $T = 1500$,

$$\log I' - \log I'' = 5.356$$

$$I'/I'' = 2.27 \times 10^5$$

That is, at $T = 1500$, the electron emission from thoriated tungsten is 227,000 times as great as that from pure tungsten.

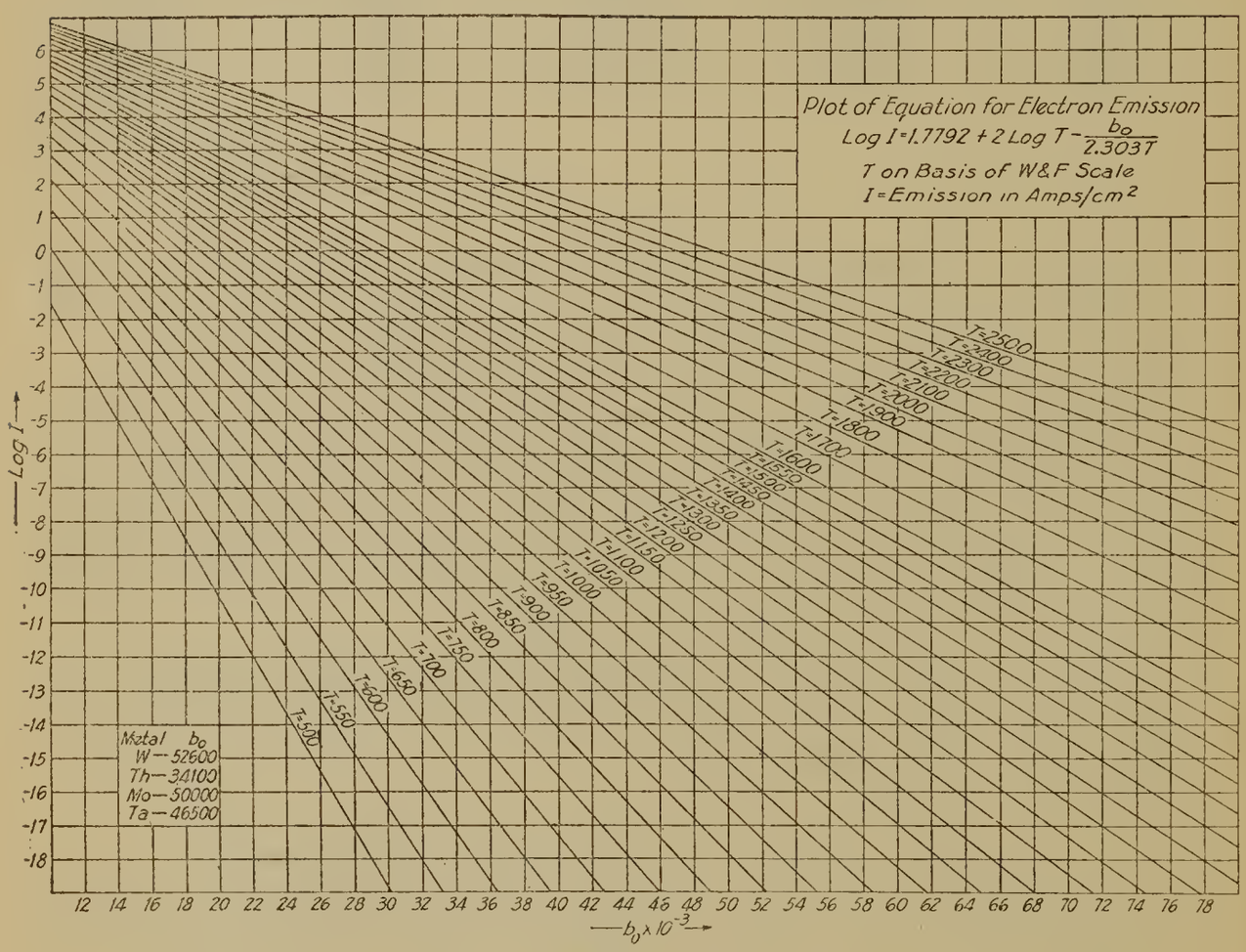

FIG. 2
Plot of Equation for Electron Emission.

Values of b_0 for different substances as determined in this laboratory are given in Table II.[16] The values for tungsten and thoriated tungsten are probably accurate to within 0.5 per cent. In the other cases, the degree of accuracy varies between 1 and 2 per cent, as the radiating properties of these surfaces have not

[16] The value for Caesium was published by I. Langmuir and K. H. Kingdon, Science, 57, 58 (1923). Some of the other values are slightly different from those published by the writer in the Physical Review, but this is due to more recent data on the radiant emissivities of the metals.

been investigated with nearly the same care as in the case of tungsten.

The physical significance of b_0 has, naturally, been the subject of considerable speculation. The energy required to evaporate one mol of electrons from a surface is given by the quantity, $L_0 = Rb_0$ (in calories). Richardson pointed out that this energy consumption is due "to the work done by the electron against the attraction of its image in the conductor" and may therefore be expressed as a potential difference, Φ_0, where

$$\Phi_0 = \frac{Rb_0 \times 4.184}{F} \text{ v.} = 8.62 \times 10^{-5} b_0 \text{ v.} \qquad (9)$$

This quantity is also known as the electron affinity or work function for emission. W. Schottky[17] and I. Langmuir[18] have both applied the theory of electric images to calculate the distance, x_0, at which an electron leaving the metal begins to be attracted by the charge induced on the surface in accordance with Coulomb's law. According to this theory

$$\Phi_0 = \frac{e}{2\,x_0} = \frac{7.16 \times 10^{-8}}{x_0} \text{ v.} \qquad (10)$$

where e is the charge on an electron, and x_0 is expressed in cm.

The third column in Table II gives values of Φ_0 and the fourth column corresponding values of x_0. It is of interest to compare the latter with the values of the atomic diameter, σ. The fifth and sixth columns give respectively the values of σ and x_0/σ. While the atomic diameters for a number of elements have been obtained by X-ray measurements,[19] it has been considered advisable for the purpose of comparison, to calculate σ from the atomic volume, V, by the relation

$$\sigma = \left(\frac{V}{N}\right)^{1/3} = 1.33 \times 10^{-8}\ V^{1/3} \text{ cm.} \qquad (11)$$

where $N = 6.062 \times 10.^{23}$

In general it is seen that for the highly electropositive elements x_0/σ tends towards the value unity while for elements of low

[17] W. Schottky, Physikal Zeit. 15, 872 (1914); *ibid.* 20, 220 (1919); Z. f. Physik. 14, 63 (1923).

[18] See foot note 4.

[19] A. W. Hull, Jr. Frank. Inst. 193, 189 (1922).

atomic volume this ratio tends towards a value of 0.56 or slightly lower. That is, b_0 (and correspondingly, Φ_0) is relatively low for the very electropositive elements, and its value increases with decrease in electropositive characteristics. Furthermore, b_0 (or Φ_0) seems to be a periodic property of the elements, but more data must be obtained before any reliable conclusions can be drawn regarding the relation between the electron affinity and the other properties of the atom.

From the form of equation (2) and also from an inspection of Fig. 2 it is seen that the lower the value of b_0, the higher the value of the election emission at any given temperature. But b_0 is not the only factor which is of significance in the practical applications of electron emission phenomena. As well known, the energy radiated from any surface increases with the temperature. For a perfectly "black body" the energy radiated, in watts per cm^2 is given by the relation

$$E = ST^4 = 5.722 \times T^4 \times 10^{-12} \text{ watts/cm}^2 \qquad (12a)$$

For any other surface, the energy radiated is less at any given temperature, so that

$$E = \alpha S T^4 \qquad (12b)$$

where α is a constant whose value varies for different substances (and also with the temperature), from 0.1 approximately to 0.9.

Combining equation (2) with (12b), it follows that the efficiency of electron emission in terms of amperes emission per watt of energy radiated,

$$\frac{I}{E} = \frac{60.2\ \epsilon^{-b_0/T}}{\alpha\ S\ T^2} \qquad (13)$$

Thus, in comparing two substances for which b_0 is approximately the same, that surface for which α is lower, is also the more efficient electron emittor.[20]

There is one more factor which is of importance from the practical point in view. This is the *volatility* of the metal. Although b_0 for the alkali and alkaline earth metals is fairly low,

[20] See foot note 15.

their relatively low boiling points would make them unsuitable for use in electronic devices. Thus it is necessary that efficiencies of electron emission for difference surfaces should be compared at the maximum operating temperatures.

TABLE II.

Values of b_0, Φ_0, x_0, and x_0/σ *for Different Metals*

Metal	b_0	Φ_0	$x_0 \times 10^8$	$\sigma \times 10^8$	x_0/σ	N
Caesium	16,000	1.38	5.19	5.48	0.95	55
Calcium.....	26,000	2.24	3.20	3.96	0.81	20
Thorium.....	34,100	2.94	2.44	3.68	0.66	90
Cerium.....	35,600	3.07	2.33	3.63	0.64	58
Yttrium.....	37,000	3.19	2.24	3.80	0.59	39
Zirconium.....	38,000	3.28	2.18	3.22	0.68	40
Uranium.....	38,000	3.28	2.18	3.09	0.71	92
Molybdenum...	50,000	4.31	1.66	2.93	0.57	42
Tantalum.....	51,000	4.40	1.63	2.95	0.55	73
Tungsten.....	52,600	4.53	1.58	2.83	0.56	74
Platinum.....	62,700	5.40	1.33	2.78	0.48	78

Effect of Surface Conditions and Field Strength on Electron Emission.

Equation (7) was derived on the assumption that the electric field strength at the cathode is zero. It is of considerable interest to inquire into the effect on the emission of varying this field strength. In the present connection we shall leave out of consideration effects due to mutual repulsion between the electrons (space charge effects). It was shown by W. Schottky on the basis of the electrical image theory mentioned previously, that if I_0 denotes the electron emission at zero field strength, and I_V denotes the emission corresponding to a field strength dV/dx at the cathode, then

$$I_V = I_0 \epsilon^{\frac{4.39}{T}\sqrt{dV/d\,x}} \qquad (14)$$

If the cathode consists of a filament of radius r, along the axis of a cylindrical anode of radius R, the value of the gradient at the cathode is given by the relation

$$\frac{dV}{dx} = \frac{V}{r \ln R/r} \tag{15}$$

where V is the voltage applied on the anode.

In the case of electrodes of different shape and relative arrangement,

$$\frac{dV}{dx} = kV \tag{16}$$

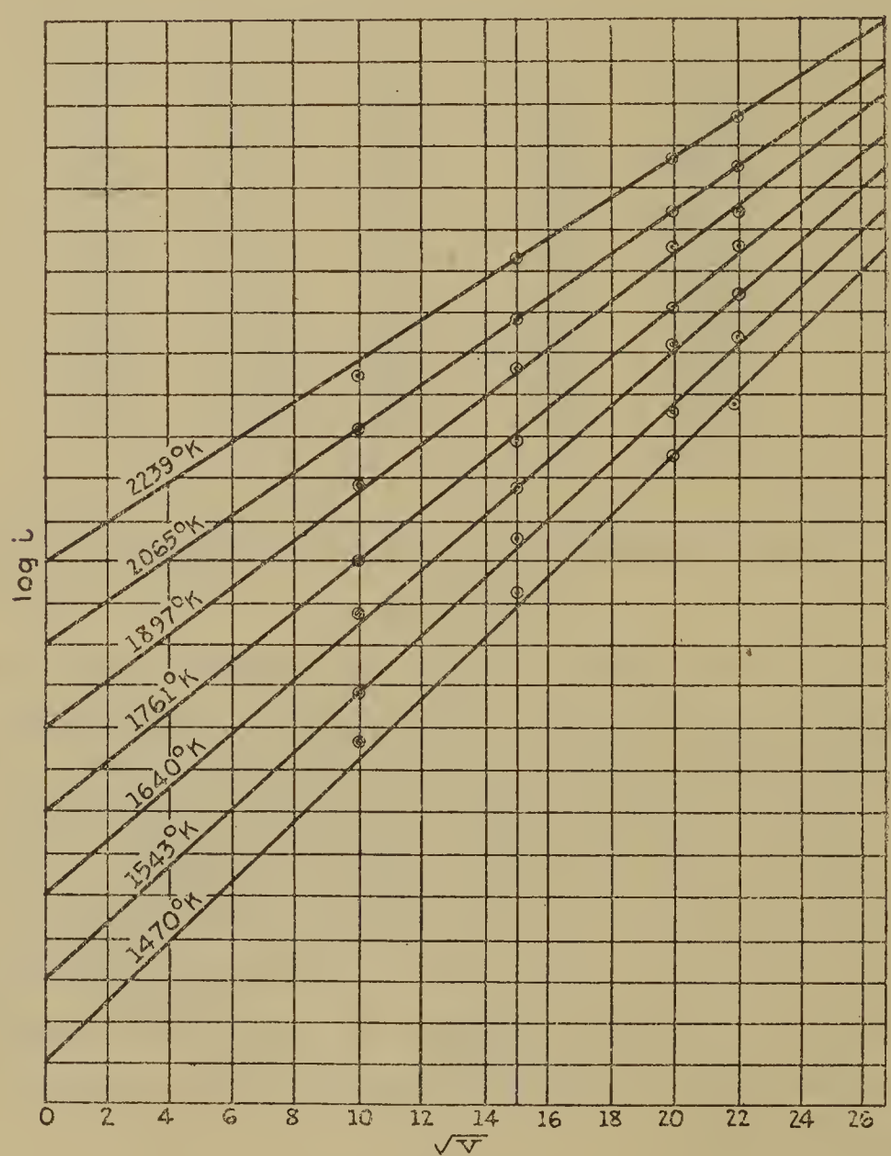

FIG. 3.

Plot of log i against $\sqrt{V}$ for different temperatures. The lines correspond to the relatives slopes, but not the absolute values of log i.

where k is a constant for the particular device. Thus k corresponds to what Langmuir has designated the "shape factor" in the case of heat conduction phenomena.

Equation (14) can therefore be written in the form

$$\log I_V = \log I_0 + \frac{4.39}{2.303\ T} \sqrt{kV} \qquad (17)$$

From this equation it follows that for the same arrangement of electrodes,

$$\frac{2.303\ T}{4.39} \frac{\triangle \log I_V}{\triangle \sqrt{V}} = \sqrt{k} = \text{constant} \qquad (18)$$

where $\triangle \log I_V / \triangle \sqrt{V}$ denotes the slope of the straight line obtained by plotting $\log I_V$ against $\sqrt{V}$.

TABLE III.

Effect of Anode Voltage on Emission

T	$\frac{\triangle \log I}{\triangle \sqrt{V}}$	T $\frac{\triangle \log I}{\triangle \sqrt{V}}$
1470	0.0070	10.29
1543	0.0068	10.51
1640	0.9065	10.66
1761	0.0063	11.09
1897	0.0054	10.21
2065	0.0053	10.95
2239	0.0050	11.20
		Av. = 10.70

Table III and Fig. 3 show a series of data of this nature obtained with a V-shaped tungsten filament in a cylindrical anode. It will be observed that the product $T \triangle \log I_V / \triangle \sqrt{V}$ is practically constant.

The effect of the increased field strength at the cathode is evidently the same as that of decreasing b_0, the work-function for emission. This is also shown by combining equation (14) with equation (7). The electron emission per unit area at any voltage V is given by the derived relation

$$I_V = 60.2\ T^2 \epsilon^{-\frac{(b_0 - 4.39 \sqrt{kV})}{T}} \qquad (19)$$

In order to show the magnitude of this decrease in b_0, values of the expression $4.39 \sqrt{kV}$ are given in Table IV, for different

sizes of filaments in cylindrical anodes, assuming an anode voltage of 100.

TABLE IV.

Decrease in b_0 at $V = 100$ for Filament in Axis of Cylindrical Anode.

Diam. of filament in cm.	Diam. of anode in cm.	$4.39 \sqrt{100\ k}$
0.001	1.00	747
0.005	0.50	409
0.005	1.00	381
0.01	1.00	289
0.1	1.00	129

Considering the first case given in this Table for which the decrease in b_0 is 747, it follows that at $T = 2000$, the emission at $V = 100$, would be 1.452 times as great as that at $V = 0$, while at $V = 10{,}000$, the ratio of emission would be increased to 41.9. At $V = 100$, the field strength at the cathode in this case is $\frac{dV}{dx} = 100\ k = \left(\frac{747}{4.39}\right)^2 = 2.894 \times 10^4$ volts/cm. and for $V = 10{,}000$, $\frac{dV}{dx} = 2.894 \times 10^6$ volts/cm.

Such field strengths can of course be attained by sufficiently high voltages on the anode, but it is also evident that the presence of a very rough surface on the cathode will tend to increase the actual field strength at projecting points in the presence of even a comparatively low voltage.

As has been shown in a very recent paper by W. Schottky,[21] the effect of microscopic projections on the surface is to increase the potential gradient at such points to more than ten times that on the plane surface.

In this manner it is possible to account for rather large values of k which may obtained in connection with measurements of the effect of increasing anode voltage on the emission. Thus, if several filaments of the same diameter are compared under other-

[21] See foot note 17.

wise similar conditions, the fact that some one wire shows a much larger value of k may be taken as indicating the presence of a much rougher surface in this case. For instance, in investigating the emission from a particular sample of molybdenum, the value of k was found to be several times greater than that obtained with other samples of similar diameter. On aging the filament for a long time, it was observed that k decreased considerably so that finally it approached the same value as that obtained for the other wires. This was no doubt due to a change in the structure of the surface.

Whether Schottky's theory is valid for very high voltages is still open to question. An investigation on this problem has been started in our laboratory.

A great deal of discussion has been aroused from time to time regarding the possibility of pulling electrons out of metals at ordinary temperatures by the application of very intense field strengths. If we eliminate the possible effects of positive ions, that is, assume that such a phenomenon may occur in an extremely high vacuum, we can calculate on the basis of Schottky's theory the field strength required.

Assume $T = 300$, and that it is desirable to obtain a current of the order of magnitude of 10^{-3} amp./cm^2 at this temperature. Substituting in equation (19) we find that

$$b_0 - 4.39 \sqrt{\frac{dV}{dx}} = 6726$$

and

$$\frac{dV}{dx} = \left(\frac{b_0 - 6726}{4.39}\right)^2$$

For a thoriated tungsten surface, $b_0 = 34{,}100$. Hence $\frac{dV}{dx} = 10^7 \times 3.9$ v./cm. This field strength could be obtained in the case of a filament 0.001 cm. diameter placed along the axis of a cylindrical anode 1 cm. diameter by applying about 135,000 v. With a cathode for which b_0 is less than that for thorium, the voltage required would obviously be lower. Thus it may be possible by means of practical high voltages to obtain "cold cathode" emission.

In conclusion it may be pointed out that on the basis of

equation (19) it follows that with cathode field strengths so intense that b_0 is decreased to approximately zero, $I_V = 60.2\ T^2$. That is, under these conditions the electron emission would no longer follow an exponential law. An experimental investigation of this nature would therefore furnish an interesting test of the validity of the equation for electron emission presented in this paper.

DISCUSSION.

LEON MCCULLOCH[1]: Some remarks that Dr. Irving Langmuir made at a symposium on "Theories of Chemical Action" before the Faraday Society in England,[2] called attention to a certain uniformity that exists among a number of physical phenomena in regard to their increase with temperature. That is, the logarithms of these phenomena plotted against the reciprocal of the absolute temperatures result in straight lines. As examples, he mentioned the vapor pressures of pure substances; the rate of evaporation; the velocity of chemical reaction, the expansion of a glass rod, as well as its electrical conductance; and, finally, black body radiation. For some reasons he did not include the emission of electrons from heated bodies. We conclude, however, from the published data on thermionic emission from metals, and from measurements upon oxide-coated filaments, that electron emission likewise obeys this law of increase with temperature.

We can then simplify the equations of Richardson and Dushman by making the term "n log T" equal to zero. We have then an equation of the form "$\log I = \log A - b/T$." If we plot values of "n log T" against "I/T", we obtain essentially straight lines for the temperature range over which thermionic emission is measured. For this reason, the presence of "n log T" has no appreciable effect upon the shape of the curves.

[1] Res. Dept., Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.
[2] Trans. Faraday Soc. 17, part 3, 600 (1922).

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

IONIZATION AND ACTIVATION OF GASES.[1]

By K. T. Compton.[2]

Abstract.

During the passage of an electric discharge through a gas the atoms are not all in the normal state, but exist in a great variety of conditions of partial or complete ionization, each state having its own characteristic physical and chemical properties. The following effects of some of these properties are important: Formation of unusual temporary chemical compounds; spectroscopic changes, especially in the band and absorption spectra; production of arcs at abnormally low voltages; catalytic action of a gas whose atoms are in an excited state upon another gas with which it is mixed. This catalytic action may be a photochemical action or not, depending on whether light or another agent is used to put atoms into the excited state.

It seems scarcely necessary, in this symposium, to review the stages by which we have come to our present knowledge of ionization of gases, for these developments, though recent, are well known and have been well summarized by Hughes[3] and by Foote and Mohler[4]. Gases may be ionized in a number of ways, as by the photoelectric effect of short wave length radiation, by impact of high-speed electrons, by high temperature and by certain chemical reactions. The present discussion has to do, however, not so much with these processes of ionization as with certain accompanying phenomena which may give to the gas new

[1] Manuscript received June 20, 1923.
[2] Dept. of Physics, Princeton University, Princeton, N. J.
[3] "Report on Photoelectricity," National Research Council Bulletin.
[4] "Origin of Spectra," Chemical Catalog Company.

properties and which must be taken into account in any effort to arrive at an adequate explanation of conduction and radiation in gases.[5]

It is becoming increasingly realized that many of the most striking spectroscopic and electrical properties of gases are due to the presence of excited, or partially ionized, atoms. Among such properties the following may be mentioned:

1. Molecular compounds of monatomic gases, and even inert gases like helium. In electric discharge tubes, positive ray analysis has revealed the existence of diatomic molecules of metallic vapors and of the inert gases, compounds of hydrogen with these gases, and other compounds which do not seem to follow the ordinary laws of chemical valency, and which have too temporary an existence to be detected by any chemical means.

2. Effect of ionization in changing chemical and spectroscopic properties of a substance to the type characteristic of the next group in the periodic table. A spectroscopic illustration is the similarity of the spectra of the ionized alkaline earths, the doubly ionized elements of the third group and the neutral alkali metals. Chemical illustrations are shown in the bivalent nature of singly ionized aluminum, the oxygen-like compounds of ionized halogens and the series of valency behaviors of carbon corresponding to its various stages of ionization—all shown unmistakably by positive ray analysis.

3. Band spectra of metallic vapors and monatomic gases. It is a generally accepted theory that monatomic elements give only line spectra, band spectra being due to molecular disturbances. Thus band spectra in normally monatomic gases indicate that molecular compounds are being formed by the agent which is exciting the spectrum. In the case of helium, for instance, the work of Compton and Lilly,[6] and of Lenz[7] has shown that the band spectrum appears only under conditions in which excited atoms are present in large concentration; Franck and Knipping[8] have shown the reasons for the formation of molecules of He_2

[5] A somewhat more complete discussion of these phenomena is being published in the Journal of the American Optical Society.

[6] Astrophys. Jour. **50**, 1 (1920).

[7] Verh. d. D. Phys. Ges., **21**, 632 (1919).

[8] Z. f. Phys., **1**, 320 (1920).

under these conditions; Curtis[9] has shown that such molecules account theoretically for the observed nature of the helium band spectrum.

4. Absorption of subordinate series lines. Monatomic gases and vapors usually show optical absorption of principal series lines. When excited atoms are present, subordinate series lines also are absorbed and may be re-emitted as resonance radiation. Striking examples of this are shown in the work by Paschen[10], who showed that the subordinate series line 10830 Å of helium becomes a resonance line if a weak electrical discharge is passed through the gas; by Füchtbauer[11], who proved that mercury vapor will absorb and re-emit the mercury lines of the visible spectrum if the vapor is, at the same time, exposed to the light 2536 which is able to produce excited mercury atoms; and by Kurth[12], who observed absorption of the strong components of the mercury subordinate series lines 4358 Å and 5461 Å when the mercury vapor was subjected to bombardment by electrons which had fallen through a sufficient voltage to produce excited atoms but not to produce ionization.

5. Low voltage arcs. The only adequate explanation of arcs in monatomic gases and vapors at voltages below the ionizing potential is ionization in two or more stages, the first stage being the production of an excited atom, and the second stage the complete ionization of this atom by another electron impact. The theory of this "cumulative ionization" has been discussed by the writer in recent papers[13] and direct experimental evidence of the two stages has been obtained by Kannenstine[14] and by Webb[15].

To this list might be added phenomena of fluorescence and resonance radiation and, possibly, of photo-chemical action.

The general point of view emphasized by all these phenomena is that we are not to think of the atoms of gas, exposed to an electric discharge or to absorbable radiation, as being all in the

[9] Roy. Soc. Proc. A., **101**, 38 (1922).
[10] Ann. d. Phys., **45**, 625 (1914).
[11] Phys. Zeit., **21**, 635 (1920).
[12] Not yet published.
[13] Phys. Rev., **15**, 476 (1920); **20**, 283 (1922).
[14] Astrophys. Jour., **55**, 345 (1922).
[15] Phys. Rev., **21**, 479 (1923).

normal state, but as existing in almost an infinity of conditions, each one characterized by its own chemical and spectroscopic properties and potential energy. The relative numbers of atoms in these various conditions depend on the potential energies of these states and on the total energy of the gas and possibly, also, on particular characteristics of the states. Generally the proportion of excited atoms is very small, but this by no means indicates their unimportance, since some properties, such as emission of radiation, depend not on the number of atoms existing in a given condition at a given instant, but on the rate at which this number is changing.

A suggestive discussion of some properties of excited atoms has recently been given by Franck and Grotrian[16], who point out the tendency of excited atoms to form both homopolar and heteropolar compounds.

Homopolar compounds. An excited atom is one which has an electron displaced from its normal position or orbit to an outer orbit characterized by a higher quantum number and larger energy. Such an atom is somewhat similar to a hydrogen atom in that it possesses an electric moment, being an electric doublet in which the displaced electron is one charge and the remainder of the atom, with a resultant charge equal to that of a hydrogen nucleus, is the equal opposite charge. These hydrogen-like excited atoms would, therefore, be expected to form chemical combinations like those of hydrogen. If two excited atoms were to meet, they could unite to form a homopolar diatomic molecule like H_2. In this way, compounds He_2, Hg_2, etc., may be formed, giving rise to band spectra and a transfer of energy from the wave length of resonance radiation to the great variety of longer wave lengths associated with the elements of the band spectrum.

The concentration of such homopolar molecules, depending as it does on the union of pairs of excited atoms, should increase approximately as the square of the concentration of excited atoms —in qualitative agreement with the observation that the band spectrum of helium increases in intensity much more rapidly than does the line spectrum when conditions are made more favorable for high concentration of excited atoms. Such favorable condi-

[16] Z. f. Phys., 4, 89 (1921).

tions are intensity of excitation, high gas pressure and absence of impurities which may act either in decreasing the average time during which an atom remains in the excited state[17], or in absorbing the resonance radiation which would otherwise be passed on from atom to atom (putting each successively in the excited state) and transforming the energy of this radiation into the spectrum of the impurity[18].

Negative ions. Excited atoms possess an electron affinity and tend to form negative ions by the capture of an electron. Thus metallic vapors and the inert gases, whose atoms in the normal state appear to possess no electron affinity, do form fairly stable negative ions when in the excited state in the presence of free electrons. Thus is explained the rapid transport of such gases to the anode at high current densities[19]. The positive ions move toward the cathode. The negative ions have the same mass but larger dimensions, so that they exert more of a viscous drag on the gas and therefore cause the net flow of gas toward the anode and the increased gas density near the anode.

The stability of these negative ions is surprising. It is probably analogous to the stability of normal helium, since we have in both cases a *pair* of electrons in the outer shell—an arrangement of high stability on the atomic structure theories of Kossel, Lewis and Langmuir. Owing to this completion of the stable group of two, we should not expect these negative ions to enter into chemical combinations, but to behave chemically like normal helium.

Heteropolar compounds. An excited atom, having an electron affinity, may also satisfy it and thus complete the stable pair by sharing an electron of an unexcited atom, thus behaving like the negative constituent of a heteropolar compound. The inert gases, like helium, would not thus form compounds since there would be no more tendency for the neutral helium atom to combine with an excited atom than to combine with any other electro-negative atom such as a halogen. But in the case of metallic vapors the normal atoms behave as the electro-positive, and the excited atoms

[17] Franck and Knipping, Z. f. Phys.; 20, 481 (1919); Franck and Reiche, *ibid.*, 1, 154 (1920).

[18] K. T. Compton, Phil. Mag., 65, 750 (1923).

[19] Skaupy, Verh. d. D. Phys. Ges. 19, 264 (1919).
Hamburger, Z. f. Wiss. Photog., 18, 1 (1919).

as the electro-negative constituents of diatomic molecules like Hg_2. Such molecules possess the energy of the original excited atoms, less the energy of molecular formation. They should be permanent except as collisions so disturb the molecules as to cause them to radiate this energy as a molecular band spectrum. An examination of conditions of excitation and the nature of the spectrum indicates that such is the origin of the unresolved band spectrum of mercury. A similar explanation probably holds for metallic hydrides, such as NaH, in which the excited sodium atom is the electro-negative constituent.

In view of such possibilities, a study of the properties of excited atoms and of the conditions determining their production is of obvious interest. The writer has given a discussion of these conditions with special reference to low-voltage arcs[20], in which it was shown that the concentration of excited atoms is proportional to their rate of production, to their average time of existence, to the square of the scattering coefficient of the gas for resonance radiation, and to the dimensions of the vessel containing the gas. This treatment showed that the great majority of excited atoms are in the excited state as a result of absorption of resonance radiation, which, after its initial appearance in a gas by electron impacts or by illumination from without, is passed on from atom to atom, putting one after another into the excited state, and finally escaping from the gas. The attempts to apply this conception quantitatively indicate that the theory predicts too large rather than too small a concentration of excited atoms.

This over-success of the theory must be due to the neglect of other ways in which the energy of resonance radiation can escape from the gas besides escape across its boundaries. That there are other ways may be illustrated as follows:

Imagine a large body of pure monatomic gas, say sodium vapor, placed with an amount of its resonance radiation in a perfectly reflecting enclosure. We know that ultimately the system must come to equilibrium with its black body radiation. There must thus be some process whereby the energy of the resonance radiation is degraded into other, principally longer,

[20] Phil. Mag., **45**, 750 (1923).

wave lengths. This process may be slow, as indicated by Wood's observation that no *detectable* amount of resonance radiation, incident on a gas, fails to be absorbed and re-emitted without change of wave length.

As was pointed out in the writer's papers, the formation of compounds by excited atoms results in a transformation of energy of resonance radiation into that of the band spectrum, radiation under the influence of the fields of neighboring atoms disperses the energy over the entire spectrum, and the presence of forign gas molecules provides a potent means of transformation of resonance radiation by its photoelectric ionizing action or by the formation of additional types of radiating compounds.

RADIATIONLESS TRANSFERS OF ENERGY FROM EXCITED ATOMS.

Another means of transformation of resonance radiation and control of the concentration of excited atoms has been suggested by Klein and Rosseland and carried to interesting theoretical and experimental conclusions by Franck and Cario. Recently Klein and Rosseland[21] pointed out the probable occurrence of a hitherto neglected effect of collisions between free electrons and atoms or molcules. We know that such collisions may result in excitation or complete ionization of the molecules if the electrons collide with sufficient kinetic energy. Conversely, Klein and Rosseland show that when free electrons collide with excited atoms, we should expect some of these atoms to revert to the normal state not by the usual process of radiation, but by a transfer of the stored-up energy of the excited atoms to kinetic energy of the colliding electrons. Thus the process of excitation of atoms by electron impacts is a reversible one.

Franck[22] immediately pointed out that the same argument could be used to prove the reversibility of excitation by atomic impacts, as in high-temperature ionization, and showed how such radiationless transfers of energy from excited atoms to neutral atoms give an adequate explanation of the effect of admixed foreign gases in reducing the fluorescence of gases like iodine or mercury vapors when they are stimulated by ultraviolet light.

[21] Z. f. Phys., 4, 46 (1921).
[22] Z. f. Phys., 9, 259 (1922).

The most interesting results of this theory are those of Cario[23] and of Franck and Cario[24]. Cario illuminated a mixture of mercury and thallium vapor with the ultraviolet mercury line 2536.7 Å, which is capable of putting mercury atoms, by which it is absorbed, into the excited state, but which is without effect on thallium vapor alone. In the mixture, the thallium became also strongly excited and emitted those lines of its spectrum which would be expected if the excitation were due to the transfer of the energy of the excited mercury atoms to the thallium atoms. Similar results were obtained in a mixture of mercury and silver vapors.

Obviously such experiments can only give positive results if the energy of the excited state of the exciting gas is greater than the energy required to produce the first displacement of an electron from its normal position in the gas which is to be thus indirectly excited. Thus the method could be used to fix this critical energy of any gas between limits corresponding to the energies of the excited states of other exciting gases which might be mixed with it.

Franck and Cario next tested the possibility of utilizing the energy liberated in these radiationless transfers at collisions of the second kind to produce chemical action. For this purpose they placed hydrogen and liquid mercury in a quartz bulb and illuminated with mercury 2536.7 Å radiation from a cooled quartz mercury arc. When the bulb was cooled, thus eliminating mercury vapor, or when the 2536.7 Å radiation was cut out by absorption screens, the hydrogen was not influenced. But with mercury vapor present, illuminated by 2536.7 Å radiation, hydrogen was dissociated into atomic hydrogen. The degree of dissociation was estimated in several ways: by the reduction of tungsten oxide, by the reduction of copper oxide, and by the reduction in gas pressure due to these chemical actions or to the "clean up" effect in which atomic hydrogen is adsorbed by the walls of the apparatus.

In this case the mercury may be looked upon as a catalizer,

[23] Z. f. Phys., **10**, 185 (1922).
[24] Z. f. Phys., **11**, 161 (1922).

or as a sensitizer, playing the same role as does the red dye sensitizer on a photographic plate. The two essentials of the above process are (1) the admixture with the hydrogen of a gas whose excited state possesses sufficient energy to dissociate hydrogen molecules, and (2) an agent which puts atoms of this gas into the excited state.

CONCLUSION.

There can be no doubt of the great importance of excited atoms in spectral excitation and in many phenomena of electric discharges in gases. Although the behavior of excited atoms at collisions with electrons or neutral atoms has been suggested rather than conclusively demonstrated by the argument of Klein and Rosseland, yet the striking success of this theory in interpreting and suggesting optical and photochemical phenomena at the hands of Franck and his co-workers demonstrates the importance of this point of view and gives hope that it may be further used and developed. The field of electrical discharges and spectral excitation is so complicated that this successful co-ordination of several diverse phenomena is an important contribution to the subject.

DISCUSSION.*

H. A. McIlvaine[1]: I have observed several things in the production of vacuum tubes which may have a definite bearing on this subject and the previous one on the "clean up" of gases by a "getter."

Without going into detail, I wish to present a few observed facts which might possibly be explained by a theory that excited atoms deposit in polarized layers, caused by permanent or transient equilibrium compounds of inert gases, etc., the molecules bearing a charge, or the outer shell electrons of the material being

* In the absence of the author, the above paper was presented by F. G. Cottrell.

[1] National Lamp Wks., General Electric Co., Cleveland, Ohio.

otherwise arranged to give such charged layers, which deposit on the walls of the container or the electrodes of the tubes.

For example, if we bombard the plate of a vacuum tube with a potential of 1500 d. c. (between filament and plate) and thus vaporize magnesium and phosphorus from the anode, several phenomena, most of which are not noticed in a two electrode lamp, result. Thus the output impedance of the tube is increased greatly (possibly two or three times that calculated from the old standard impedance formula having only electrode sizes and spacing as its variables). By subsequent heating of the bulb and rebombardment of the plate, the output impedance may be lowered from a possible 50,000 ohms (at a definite E_P) to a value as low as 15,000 ohms, assuming the latter value to be calculated from the old formula, or to some higher value.

Briefly, the following are some of the facts noted: (1) A slight "clean up" of the inert gases is noted possibly due to small formation of such negative ions. (2) Under certain conditions, a "getter" gives up its gas again. (3) Gases in the "excited" state seem to unite with the walls of the container when no "getter" is present. (4) Gaseous "clean up" occurs almost always only after the gas is ionized. (5) Electron emission from filaments is affected by gaseous vapors. (6) The space charge between electrodes, and, therefore, the input impedance, output impedance, and amplification constant (and consequently mutual conductance), at a given plate and grid potential, is changed, probably due to a change in contact potential difference between the surfaces.

It has been shown by the positive ion deflection method that temporary charged compounds of inert gases, etc., exist, and the above facts indicate that there may be deposited on the walls of the container and electrode surfaces charged layers of some such nature.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

ELECTRICITY IN FLAMES.[1]

By H. A. Wilson.[2]

Abstract.

This paper contains a concise review of the present state of knowledge of the subject, followed by a bibliography. It is divided into the following sections: (1) Early observations; (2) Conductivity of salt vapors in flames; (3) Ionic mobilities; (4) Flames in a magnetic field; (5) Charge carried by the ions of salt vapors at high temperatures; (6) Conductivity of flames for rapidly alternating currents; (7) Thermodynamical theory of ionization at high temperatures; (8) Bibliography.

The fact that flames and the gases coming from them possess electrical conductivity has been known for more than a hundred years and the subject has been investigated by very many physicists. The earlier experimenters obtained many interesting results, but were not able to explain them since no satisfactory theory of gaseous conductivity was available.

In 1882 Giese developed the ionic theory of gaseous conductivity and showed that many of the properties of the gases coming from flames could be explained by means of it. Giese's work is important since it is the first in which the ionic theory of gaseous conductivity is definitely put forward.

The principal results obtained before Giese's theory appeared may be summarised as follows:

1. Two electrodes at different temperatures in a flame give a

[1] Manuscript received June 18, 1923.
[2] Rice Institute, Houston, Texas.

current through a galvanometer from the hotter to the colder electrode in the flame.

2. The current, due to a battery, between two electrodes symmetrically placed in a flame is greater the higher the temperature of the electrodes.

3. The current between two electrodes due to a battery is unaffected by moving the positive electrode about, so long as it remains red hot, but depends greatly on the position and temperature of the negative electrode.

4. Salts of the alkali and alkaline earth metals increase the conductivity.

5. A bead of salt increases the current greatly when put in at the negative electrode but has little or no effect at the positive electrode or between the electrodes.

6. With two electrodes in a flame connected to a battery giving several hundred volts and a third electrode connected to a gold leaf electroscope, the electroscope indicates the same potential as when connected to the positive electrode. If the positive electrode is connected to the earth the electroscope collapses but if the negative electrode is earthed the electroscope indicates a positive charge.

It was concluded from (3) (5) and (6) that the greater part of the resistance of the flame to the passage of a current between two electrodes in it is located close to the negative electrode. Later work has confirmed this conclusion.

An important paper by Arrhenius on the conductivity of the Bunsen flame containing salt vapors appeared in 1891. Arrhenius's results have been confirmed and extended by Smithells, Dawson and the writer. The main results of these investigations may be summarized, as follows:

The current c between two electrodes (both at a high temperature) in the flame due to a potential difference V is given approximately by the equation

$$Ak^{-\frac{1}{2}}dc + \alpha A^2 k^{-1} c^2$$

where d is the distance between the electrodes, k the concentration of the salt vapor in the flame and A and α are constants. The

constant α has the same value for all alkali metal salts and A has the same value for all salts of any one alkali metal but diminishes as the atomic weight of the alkali metal increases.

Thus if V and d are kept constant then the current varies as the square root of the concentration of the salt. When d is small and V not too small the equation becomes approximately

$$V = \alpha A^2c^2/k$$

so that the current varies as $\sqrt{kV}$.

The term $Ak^{-1/2}$ d c is found to represent the fall of potential in a uniform potential gradient proportional to the current and extending over most of the distance between the electrodes. The term $\alpha A^2k^{-1}c^2$ represents rather sudden drops of potential at the electrodes, that at the negative electrode being much the greater. Since for any alkali metal the current is independent of the acidic constitutent of the salt it follows that chemical action or dissociation or both convert the metal into the same state whatever salt is vaporized. Arrhenius supposed that all salts are converted into hydroxides which then dissociate partly into positive metallic ions and negative hydroxyl ions. The writer has come to the conclusion that all salts are converted into metallic vapor which partly dissociates into positive metallic ions and negative electrons. The main reason for this conclusion is that the negative ions are found to have a much greater velocity than the positive ions.

The metal vapor gives rise to equal numbers of positive and negative ions so that the electrical properties of the flame must depend on the number of ions present and on their mobilities. For flames of equal conductivity containing different alkali metals the relation between the current, potential difference and distance between the electrodes is nearly the same. This means that the constant α in the equation $V = Ak^{-1/2}\ d\ c + \alpha A^2k^{-1}c^2$ has nearly the same value for all alkali metals. It follows from this that all alkali metals give ions having the same mobilities. Close to the negative electrodes the current is carried by positive ions and close to the positive electrode by negative ions. The fact that the fall of potential at the negative electrode is much greater than

that at the positive electrode therefore indicates that the mobility of the negative ions is much greater than that of the positive ions.

The equation connecting V k and c indicates that c should be zero when k is zero, which is not quite true, because there is a small current through the flame when no salt is present. When k is not very small the ions due to the flame gases can be neglected and we have an equilibrium between ionization and recombination so that the conductivity varies as $\sqrt{k}$ as indicated by the equation given above, but when k is very small the ions due to the flame gases cannot be neglected and the theory indicates a more complicated relation between the conductivity and k.

If k denotes the concentration of the alkali metal vapor and c the conductivity measured by the ratio of the current to the uniform potential gradient between the electrodes then

$$K = \frac{c^2 - 1}{c} (b + ac)$$

where c is taken equal to unity when $k = o$ and a and b are constants. The constant b is the same for all alkali metals and a is proportional to the concentrations giving equal conductivities. This equation deduced from the ionic theory is found to agree with the experimental results. When c is large it becomes $k = ac^2$. The fraction of the metal ionized is equal to $b/(b + ac)$ and so can be calculated from the values found for b and a. The percentage of alkali metal vapor ionized in a Bunsen flame when the concentration is very small is found, in this way, to have the following values: Caesium, 91; Rubidium, 69; Potassium, 58; Sodium, 1.6; Lithium, 0.2.

The large relative concentrations of the alkali metals giving equal conductivities in a Bunsen flame are found to be as follows: Lithium, 4300; Sodium, 626; Potassium, 7.3; Rubidium, 4.5; Caesium, 1.0.

The Ionic Mobilities

A great many attempts have been made to determine the mobilities of the ions in flames. The writer found that all alkali

salts give ions having nearly the same mobilities, that of the negative ions being very much the greater, but no accurate method has been discovered, and the results obtained by different observers differ greatly. The velocity of the negative ions due to 1 v. per cm. in a Bunsen flame appears to be between 1000 and 20,000 cm. per sec. The most likely value is perhaps about 7000 cm. per sec. The velocity of the positive ions due to 1 v. per cm. appears to be only 1 or 2 cm. per sec. It was first suggested by Lenard that the negative ions must be electrons at least during a part of their existence. It may be that in very hot flames when the electric field is not very small they are electrons all the time but in cooler flames and weak electric fields the electrons may combine with neutral atoms for a part of the time. This may account for the very different values of the mobility obtained by different observers.

Ionization by Collisions in Flames

G. Moreau has shown that with strong electric fields ionization by collisions of the electrons with alkali atoms in flames occurs and he has investigated this effect and obtained interesting results.

Flames in a Magnetic Field.

The Hall effect in a Bunsen flame containing alkali metals has been investigated by Marx and the writer. The results obtained indicate that the mobility of the negative ions is greater than that of the positive ions by several thousand cm. per sec. for 1 v. per cm. If the theory of the Hall effect in gases could be worked out satisfactorily the measurement of the Hall effect would enable the mobility of the negative ions to be found accurately.

The effect of a magnetic field on the conductivity of the Bunsen flame has been examined by the writer and C. W. Heaps. The results obtained indicate that a transverse field increases the resistance of the flame. Here again if the theory of this effect could be worked out satisfactorily the mobility of the negative ions might be deduced from the results.

Charge Carried by the Ions of Salt Vapors at High Temperatures.

When a current is passed through a stream of an alkali salt vapor mixed with air at a high temperature it was found by the writer that the current rises to a maximum value as the potential difference is increased and the metal is removed from the stream of air probably by deposition on the negative electrode. The maximum current was found to be equal to that required to electrolyze an equal amount of the salt in a solution. This shows that the metal ions in the hot vapor carry the same charge as in solutions.

Conductivity of Flames for Rapidly Alternating Currents.

The conductivity of a Bunsen flame containing alkali salt vapors for high frequency alternating currents has been studied by the writer and E. Gold. It was found that the effect of the salt vapor between the electrodes is to increase the apparent capacity of the electrodes. The increase in the apparent capacity calculated on the ionic theory was found to agree with that observed assuming the negative ions to be electrons.

Recently A. B. Bryan has found that the salt vapor also changes the resistance between the electrodes as well as the apparent capacity.

Thermodynamical Theory of Ionization at High Temperatures.

The dissociation of a metal vapor into ions is evidently analogous to any ordinary chemical dissociation so that we should expect the thermodynamical theory of chemical equilibrium in gases to be applicable. The thermodynamical theory was used by the writer to calculate the energy absorbed during ionization of gases and alkali salt vapors from the variation of the ionization with temperature in 1901.

An important development in the application of thermodynamics to gaseous ionization has been made recently by Saha. He assumes (1) that the energy absorbed by the dissociation of one metal atom into a positive ion and an electron is equal to the product of the ionization potential of the metal and the electronic charge. (2) that the metal atoms, positive ions and electrons

may be all regarded as perfect monatomic gases the entropies of which can be calculated from their atomic weights. The only assumption about which there is any serious doubt is that the electrons can be regarded as a monatomic gas the entropy of which can be calculated from its atomic weight. It was shown by the writer in 1903 that the variation of the thermionic emission of electrons from hot bodies with the temperature can be calculated thermodynamically by assuming the emission to be analogous to evaporation. The agreement of this calculation with the facts justified the assumption that the electrons could be treated as a gas and this has been confirmed by several subsequent investigations. Saha's theory appears therefore to rest on a firm foundation. It has been shown recently by A. A. Noyes and the writer that the ionization of alkali metals in flames is approximately in accordance with Saha's theory.

If $K = p_+p_-/p$ where p_+ denotes the pressure of the positive ions, p_- that of the negative ions and p that of the neutral metal atoms, then according to Saha's theory

$$\log_{10} \frac{K_2}{K_1} = \frac{5048\ (V_1 - V_2)}{T}$$

where K_1 and K_2 are the values of K for two metals for which V_1 and V_2 are the ionization potentials and T denotes the absolute temperature. The conductivity of the vapor is proportional to p_- because the mobility of the positive ions is negligible so that the K's are inversely proportional to the concentrations giving equal conductivities. Taking K for lithium equal to unity we get the following results at 2000° absolute.

	V (Volts)	K	C	KC
Caesium	3.873	5731	1	5731
Rubidium	4.154	1119	4.5	5000
Potassium	4.317	434	7.3	3150
Sodium	5.111	4.3	626	2690
Lithium	5.362	1	4300	4300

The third column gives the values of K calculated by means of the equation above and the values of V. The fourth column

contains the relative concentrations (C) giving equal conductivities in a flame. The last column gives the product KC which does not vary much showing that K is nearly inversely as C in accordance with Saha's theory.

A list of books and papers on electricity in flames follows. Only a few of the earlier papers are included. References to the others will be found in the books by Wiedemann and Marx. With a few exceptions, papers on the conductivity of the gases coming from flames are not included.

An attempt has been made to classify the papers. The early papers and those dealing with several topics are classified under the heading "conductivity of flames."

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A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE RELATION BETWEEN CURRENT, VOLTAGE AND THE LENGTH OF CARBON ARCS. II.[1]

By A. E. R. Westman[2] and W. J. Clapson.[2]

Abstract.

In a previous paper[3] it was shown that for currents from 300 to 400 amp. the voltage over a carbon arc is approximately equal to the arc length in millimeters, where the arc length is measured from the tip of the cathode to the bottom of the anode crater. This paper describes much more accurate measurements over a range of currents from 100 to 700 amp. The results obtained, which support the conclusions of the previous paper, are compared with those of Grotrian,[4] Nottingham,[5] and Watts.[6]

I. INSTRUMENTS AND APPARATUS.

Direct current from the university power plant and several batches of electrodes manufactured by the National Carbon Co. were used. The instruments (cathetometer, calibrated voltmeters, millivoltmeters and shunts) and the furnace are those described in the previous paper, where a general wiring diagram is also given. As the discussion in connection with the previous paper showed that this was not sufficient to enable the arrangement of the equipment to be visualized easily, a drawing of the furnace has been included in the present paper. (Fig. 2).

Voltmeter circuit. In the connection diagram (Fig. 1) the voltmeter V_2 (hereafter called the "divmeter"), which has a 3-volt scale divided into 150 divisions ("div."), was used for measuring

[1] Manuscript received May 21, 1923.
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[3] Trans. Am. Electrochem. Soc. 43, 171 (1923).
[4] Annal. d. Phys. 47, 141 (1915).
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small changes in arc voltage, and indicated instabilities in the arc before they became pronounced enough to be noticed on the voltmeter V_1 (150 volt scale). B is a two-volt storage battery, and *R_1, R_2, R_3 and R_4 are accurate resistances of the values shown in the diagram.

If D is the reading of the divmeter when the circuit is disconnected from the arc, A, Fig. 1, and the four-pole double-throw switch S is closed in the direction indicated by the arrow, the divmeter readings (div.) when the switch is reversed and the cir-

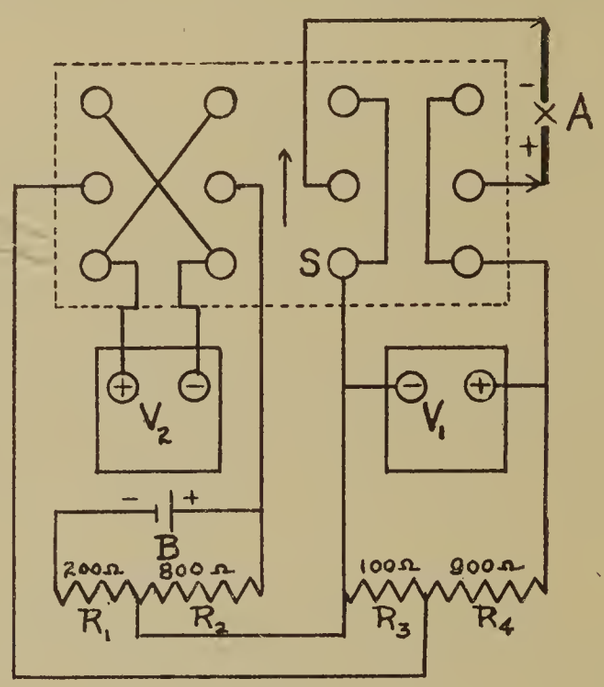


FIG. 1.

cuit is connected to the arc, will be related to the arc voltage V_1 by the relation:

$$\text{“div.”} = 2.88\ V_1 - 1.017\ D \qquad (1)$$

The factors 2.88 and 1.017 are independent of the voltage of the battery B, and D does not vary during a run.

Voltmeter Contacts. When making voltage measurements errors due to voltage drops in the electrodes were minimized by the use of graphite rods (Fig. 2) which made contact to the electrodes close to the arc. These rods were made from graphite electrodes 24 in. (61 cm.) long and 2 in. (5 cm.) in diameter; one end was threaded for 12 in. (31 cm.) to fit into graphite collars wedged firmly in the furnace wall and the other end tapered to a diameter

* The symbol Ω in diagram indicates ohms, not megohms.

of ¾ in. (2 cm.) at the point. By screwing the rods in or out, they could be kept free of the electrode during movements of the cathode or held tightly against them when voltage readings were required. The contact resistance between the two graphite rods and the electrodes was only a small fraction of an ohm, and quite negligible when compared with the resistance of the voltmeter.

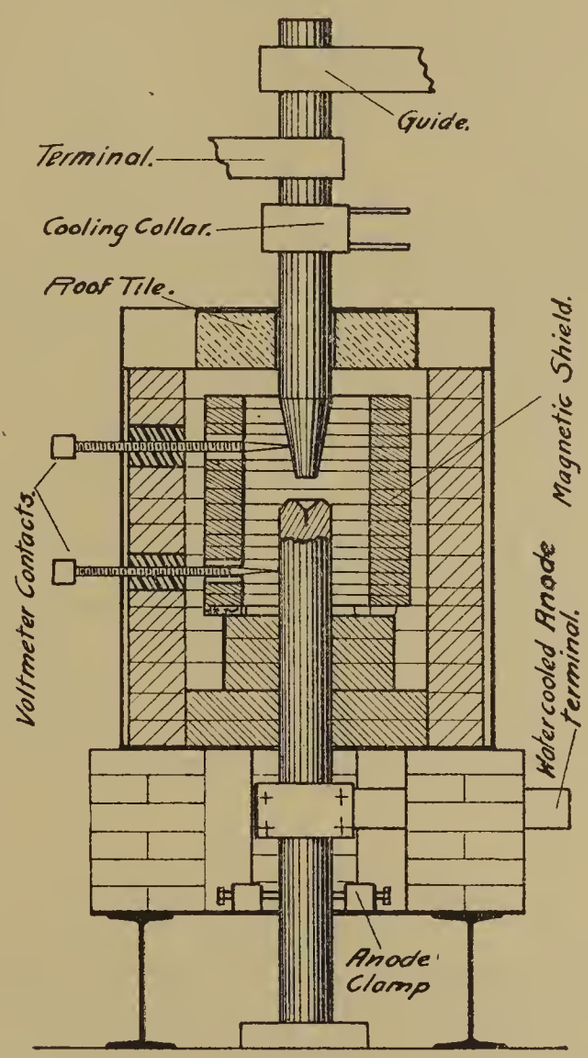


FIG. 2.
Experimental Furnace.

Anode clamp. As it was desirable to use a fresh anode, turned to the proper dimensions in the university machine shop, for each run, a clamp was made which permitted quick replacement, and at the same time permitted the anode to be quickly centered and held firmly during a run. This consisted of four steel set screws set 90 degrees apart in a plane perpendicular to the anode, and operating through four iron blocks bolted to the iron platform supporting the furnace.

Cathode guide. In order to insure smooth vertical movements of the cathode, one of the two jibs (Fig. 2) ordinarily used to operate an 80 kw. single-phase Heroult furnace was used for actually supporting the cathode, while the other, held stationary, was used as a guide.

New magnetic shield. The iron window frames which were used as a magnetic shield in most of the runs became broken and warped with use and in the last 4 or 5 runs were replaced by standard 10 in. (25 cm.) cast iron steam-pipe flanges. (Fig. 2).

Cooling apparatus. As it was impossible to make a plaster model (see later), or replace the anode after a run until the furnace had cooled, a small electric fan was arranged to send a rapid current of air through the furnace. This method proved much more effective than others that were tried, and reduced the time of cooling from 10 to about 2 hr.

Observation screen. As it was desired to record changes in the appearance of the arc during a run, and as the arc was far too bright to be observed without screens, an observation screen was used consisting of four plates of colored glass, red, amber, violet, and five sheets of mica (muscovite). This transmitted only a small band in the red part of the spectrum, about 7000 Ångström units.

II. CONDITIONS FOR A STEADY ARC.

Carbon powder for starting. As stated in the previous paper,[3] carbon powder dusted from the electrodes after a run was far better for starting and centering the arc than other kinds of finely divided carbon such as electrode filings, powdered coke, etc., and showed on analysis, about 3 per cent ash as compared with about 1 per cent for electrode filings. That this high ash content contributed to the effectiveness of the carbon powder is shown by the fact that an unsteady—*e. g.*, groaning—arc can be steadied for 2 or 3 min. by pouring about a gram of powdered silica through an iron pipe into the anode crater. This, however, has the added effect of lowering the arc voltage about 20 v. and was never used for steadying the arc when measurements were to be made.

Electrode dimensions. In the previous paper (Fig. 2, p. 179, vol. 43.) the electrode dimensions are given, which were found necessary to secure a steady 400 amp. arc. These dimensions proved unsatisfactory for 600 amp. and after many trials those shown in full line in Fig. 3 of this paper were found to give good results, but are subject to slight variations depending on the batch of electrodes used.

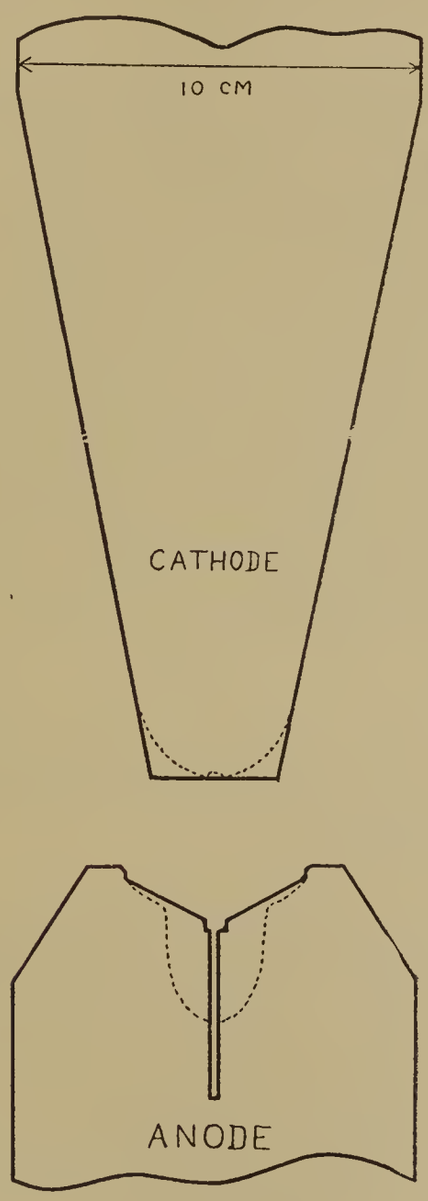


FIG. 3.

Swinging arcs. Swinging arcs, a form of instability encountered occasionally in the preliminary work, were very persistent and troublesome with these high currents. When the arc was swinging, observation showed two spots at opposite sides of the bottom of the anode crater, which appeared dark and bright alternately, at intervals of one half second or less. On cooling two

small craterlets were found where the spots had been seen, which in every case were situated on a crack. If the crack was to one side of the vertical axis of the anode, the crater deepened obliquely in that direction. A hole 5/64 in. (2 mm.) in diameter drilled in the center of the anode (see Fig. 3) was found to prevent swinging arcs and to produce symmetrical craters. After about an hour, however, groaning inevitably set in and the run had to be discontinued.

Other forms of instable arcs. With 600 amp. arcs two intermediate stages between a "groaning" and a steady arc were observed. In one, the whole rim of the anode crater became incandescent; in the other, 1 to 5 incandescent spots were seen to travel slowly, about 1 rev. per sec., around the rim; in both stages most of the arc was apparently still going into the crater. These phenomena were not accompanied by any particular sound, but the readings of the divmeter were 40 or 50 div. high and unsteady. They were invariably followed by a groaning arc, in which the anode spot oscillates between the bottom and edge of the crater, the divmeter reading being high when the arc is on the edge. The opposite was observed with 400 amp. as stated in the previous paper.

The groaning arc was sooner or later succeeded by a "shrieking" arc, which rapidly burned away the edge of the crater but did not blow out as with 400 amp.

Steady arcs. When the arc was steady, *i. e.,* was silent and gave steady divmeter readings rising at a slow uniform rate of about 1 div. per min., it appeared quite transparent and clear through the observation screen; the edge of the anode looked dark, and the small hole drilled in the center of the crater was black and distinct in outline. Any unsteadiness in the divmeter readings was invariably accompanied by a quite noticeable fogginess in the crater, through which the hole could not be seen.

With a steady arc the electrodes burned to the shapes shown by the dotted lines in Fig. 3. There was a small crater in the tip of the cathode, and the central portion of the anode crater was four or five times as deep as the rest of the crater. The diameter of this central deeper portion was approximately equal to the diameter of a brilliant core that was seen in the arc when the red

glass was removed from the observation screen, so that it transmitted some violet light. In the shallower portion of the anode crater the hollow stalagmitic structures shown in Fig. 4 were found, which on analysis appeared to be wholly graphite with only a trace of ash.

III. MEASUREMENTS.

Voltage measurements. In the runs recorded in Tables II, III, V, VII and VIII, the voltmeter leads were connected to the electrode holders, and therefore the voltage drop in the electrodes was included in the voltage readings. In order to arrive at the order of magnitude of the correction necessary, the average specific resistance of several cold carbon electrodes was determined by a Poggendorf's bridge, and found to be 0.00147 ohm per inch cube (0.000117 ohm per linear inch). The resistance of the electrodes was then calculated from their known dimensions, assuming linear distribution of temperature and applying Hansen's[7] correction for the change of specific resistance of carbon with temperature. This was checked directly by measurements of actual voltage drops in the electrodes during a run, using graphite contacts.

As these calculations gave 0.008 ohm for the resistance of the electrodes corresponding to a fall of 4.8 volts for 600 amp., the graphite contacts described above were used in the runs recorded in Tables I, IV and VI. In this way only the resistance of the last 3 or 4 in. of the electrodes had to be considered and as this amounted to about 0.0008 ohm, determined as described above, it necessitated a correction of only 0.48 v. for a current of 600 amp.

Plaster model measurements of arc length. When the arc had been steady for a half hour or so, the height of the cathode was measured by the cathetometer, the circuit was broken, powdered carbon poured on the electrodes through an iron pipe to keep them from burning away, and the cooling fan set in motion. When the electrodes were cold, not above 50 or 60° C., a mixture of plaster of paris, fire clay, and common salt, 7 : 5 : 1 by volume, with enough water to form a stiff paste, was pressed into the space between the electrodes; the cathode was then lowered to get a good impression, and the cathetometer read again. After setting,

[7] Electrochem. and Met. Ind. 7, 514 (1909).

which took only 4 or 5 min. as compared with 2 or 3 hr. for the fire clay mix previously employed, the cast was removed and measured by calipers to half a millimeter in order to determine L, the distance in mm. from the tip of the cathode to the bottom of the anode crater. Models made in this way are smooth and strong, show no change in volume on setting, and can be measured to half a millimeter.

x 20

FIG. 4.

As the plaster model could not be made until the electrodes had cooled, and as the electrodes contracted slightly on cooling, a small constant error was introduced. A correction for this small error* was obtained in the following manner.

When the average power input of 18 kw. had been maintained for the duration of an average run, the circuit was broken and a graphite plug reaching to the bottom of the anode crater was quickly inserted between the electrodes; the cathode was lowered until it just touched the plug, closing an electric bell circuit, and the cathetometer read before the plug had time to expand with the heat. The rest of the anode crater was then filled with copper turnings which melted and on cooling again solidified holding the

* This error as pointed out by Mr. J. H. Kelleher in the discussion of the previous paper.

plug in place. While cooling the cathode tip was protected from oxidation by powdered carbon.

When the furnace had cooled, the dust was blown out with bellows, the cathode lowered until the bell rang, and the cathetometer read again. As the length of the graphite plug, measured cold, was the same before and after the determination, the difference in the cathetometer readings was taken as equal to the contraction of the electrodes on cooling. Two determinations gave 1.5 mm. and 1.6 mm. respectively, so the correction was taken as 1.5 mm., which was of the same order of magnitude as that given by a rough approximation based on Fizeau's[8] results. Tables I, II and III, give the results obtained by this method

TABLE I.

Plaster Model Results.

Voltage readings, obtained with graphite contacts, corrected for 0.0008 ohm electrode resistance. Values of L corrected for 1.5 mm. contraction of electrodes on cooling.

Run.	i Amp.	e V.	L mm.	$n = \frac{e}{L}$
26	620	30.5	31.1	0.98
27	645	20.9	21.6	0.97
29	510	50.6	52.5	0.97
31	623	28.5	27.5	1.04
32	587	27.5	25.9	1.06
34	650	24.5	25.6	0.96
35	629	26.3	27.7	0.98
37	560	42.6	42.5	1.00
38	120	29.0	29.6	0.98
42	315	52.7	53.3	0.99

Average $n = 0.99 \pm 0.02$*

* $\pm$ 0.02 is the dispersion calculated from the formula $d = 0.6745 \sqrt{\frac{\Sigma(v^2)}{n-1}}$, where v is the deviation of each reading from the average, and n is the number of measurements. Tuttle, Theory of Measurements, page 215.

TABLE II.

Plaster Model Results.

Voltage readings, obtained with leads connected to the electrode holders corrected for 0.008 ohm electrode resistance. Values of L corrected for 1.5 mm. contraction of electrodes on cooling.

12 determinations, i from 400 to 700 amp. gave $n = 0.95 \pm 0.07$.

[8] C. R. 68, 1125, 1869.

TABLE III.

Clay Model Results.

Results given for current range of 200 to 400 amp. in previous paper, Table II, p. 181, Vol. 43, with voltage corrected for 0.008 ohm resistance in the electrodes, and L corrected for 1.5 mm. contraction of electrodes on cooling.

i amp.	e V.	L mm.	$n = \frac{e}{L}$
280	50.8	54.5	0.93
311	41.0	40.5	1.01
350	39.2	40.5	0.97
385	27.9	28.5	0.95
390	41.4	40.5	1.02
			Average n = 0.98 ± 0.03

Caliper measurements of arc length. A second method for determining L consisted in measuring with calipers the distance between the electrodes before a run while the furnace was cold, and noting the cathetometer reading for the first four or five minutes of a run. The value of L could thus be determined from the cathetometer reading, with a small correction for the amount burned off the electrodes as calculated from the rate of rise in voltage. As this correction was less than 2 mm. it introduced no great error, but there was always uncertainty as to whether the carbon dust, used to start the arc, had completely burned away. Tables IV and V give the results obtained by this method.

Measurement of de/dL for constant external resistance. As described in the previous paper the cathode was raised or lowered about 5 mm. every 7 or 8 min. during a run; the div., volts (e), and amperes were recorded every minute and the cathetometer read after every movement. In this way values of de/dL for constant external resistance were obtained. Tables VI, VII and VIII give the results obtained by this method.

Measurement of de/di for constant arc length. Four or five runs were made in which the current through the arc was suddenly changed, 100 amp. or so, every eight or ten minutes by varying the external resistance, the cathode held stationary and the meter

Table IV.

Caliper Results.

Voltage readings, obtained with graphite contacts, corrected for 0.0008 ohm electrode resistance.

Run	i amp.	e V.	L mm.	$n = \frac{e}{L}$
25	625	23.9	24.5	0.98
31	600	27.0	30.1	0.90
34	625	23.3	24.7	0.94
35	590	25.0	26.4	0.95
37	642	23.0	26.6	0.87
38	657	19.0	19.2	0.99
41	525	30.6	29.0	1.06
42	550	26.6	24.0	1.07
43	540	29.1	28.1	1.03
44*	577	29.3	25.2	1.16 Graphite
				Average n = 0.98 ± 0.05

* Acheson graphite electrodes used in run 44.

Table V.

Caliper Results.

Voltage readings, obtained with leads connected to the electrode holders, corrected for 0.008 ohm electrode resistance.

6 determinations, i from 400 to 650 amp. gave n = 0.89 ± 0.09

Table VI.

de/dL Results.

Voltage readings, obtained with graphite contacts, corrected for 0.0008 ohm electrode resistance.

Run No. 37, average of four results, 0.92, 1.01, 0.88, 1.03 = 0.96

Table VII.

de/dl Results.

Voltage readings, obtained with leads connected to the electrode holders, corrected for 0.008 ohm electrode resistance.

32 determinations, 500 to 650 amp. Average de/dL = 1.09 ± 0.06.

Table VIII.

de/dL Results (by Westman).

Voltage readings, obtained with leads connected to the electrode holders, corrected for 0.008 ohm electrode resistance.

43 determinations, 200 to 400 amp. Average de/dL = 1.05.

readings taken every minute. It was only when the conditions for getting very steady arcs had been thoroughly mastered that it was possible to do this without causing the arc to groan or shriek.

The results of two such runs (23 and 46) are shown graphically in Fig. 5. The divmeter readings, corrected for 0.008 ohm electrode resistance in the case of run 23, and for 0.0008 ohm in the case of run 46, are plotted against time in minutes. In run 23

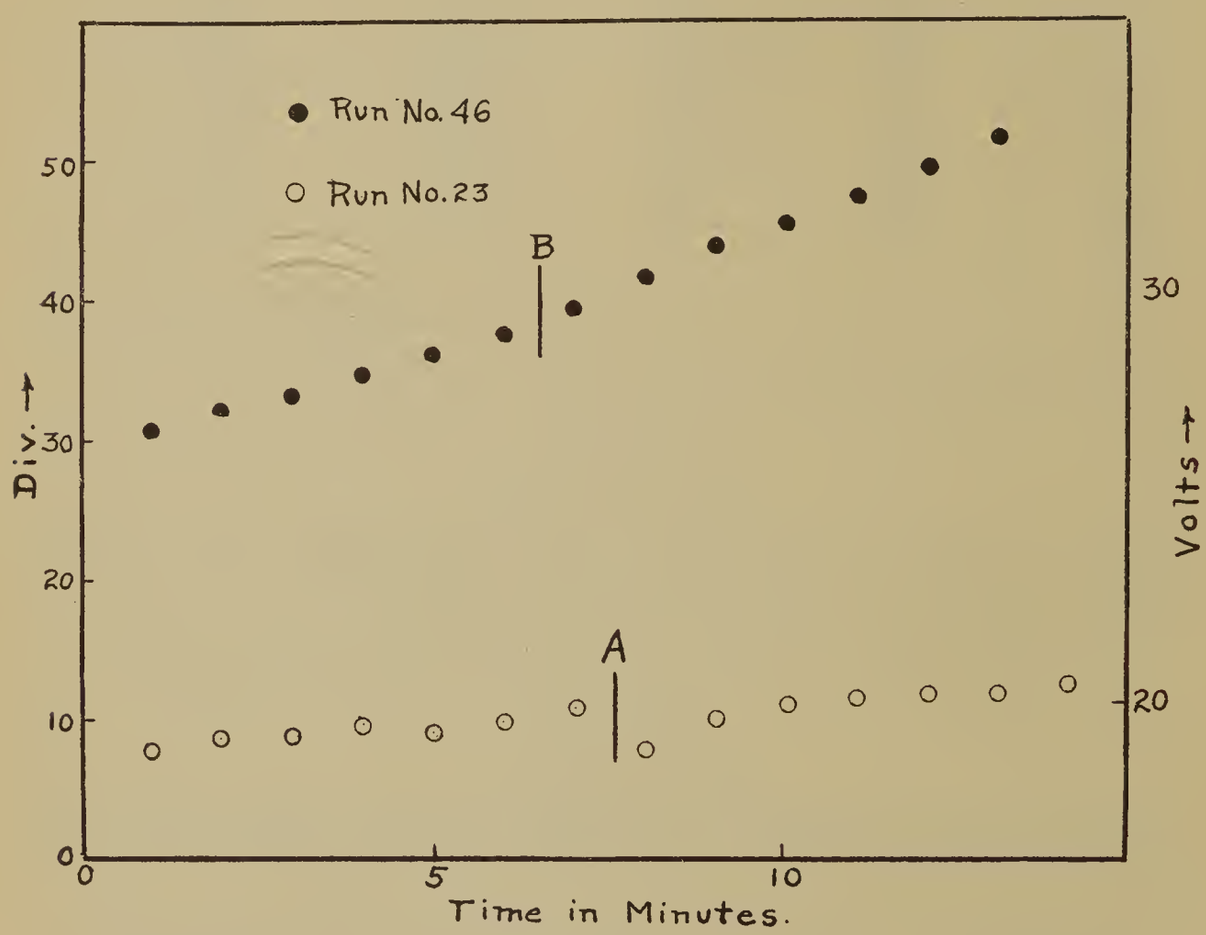


FIG. 5.

(lower) the current was decreased from 681 to 620 amp. at the point A (time = 7.5); in run 46 the current was decreased from 512 to 450 amp. at the point B (time = 6.5). It is evident from the graph that no change of voltage is caused by these changes of current, (*i. e.*, de/di = 0.) although in the case of run 46 a small increase in the rate of burning away of the electrodes is shown by the fact that the divmeter readings climb faster after the current is changed.

The results of the measurements reported in Tables I to VIII

show that the relation between current, voltage and the length of carbon arcs can be expressed by the equation

$$e = 0.99\ L \qquad (2)$$

where e is the voltage over the arc in volts and L is the length in millimeters from the tip of the cathode to the bottom of the anode crater.

IV. COMPARISON WITH OTHER EXPERIMENTERS' RESULTS.

Values of the fall in potential in the arc stream, exclusive of cathode and anode falls in the immediate vicinity of the electrodes, calculated from the formulas given by various experimenters and expressed as volts per millimeter are given in Table IX. It is interesting to note that these are comparable with the value found by us as stated above in equation 2.

TABLE IX.

Fall in Potential in the Arc Stream

Experimeter	Current Range amp.	Length Range mm.	Fall in Potential in Arc Stream v./mm.
Ayrton[9].....	0- 30	0- 7	2.07
Grotrian[4].....	0- 3	100-500	1.20
Nottingham[5]...	0- 10	0- 10	1.25 (copper cathode)
Watts[6].....	150-800	40-150	0.8 to 1.40
W. and C.....	100-700	15- 60	0.99

[9] "The Electric Arc," p. 232. Also Child, "Electric Arcs," p. 25.

As shown in Table IX the only experiments made with heavy currents besides our own are those of Watts. This author claims no great accuracy for his results, which were obtained incidentally to a study of the formation of borides and silicides. He states that when the voltage between the terminals of his furnace was about 80 v. with a current of 600 amp. the arc length was from 60 to 75 mm. Equation (2) allowing 0.011 ohm as electrode resistance (about 40 in. of 1.25 in. graphite) gives a value of L = 74 mm., which is of the same order of magnitude.

His conclusion that "an arc of fixed length tends to maintain a constant voltage" is in accordance with our results; and where he

observed differences between the behavior of his arcs and those of Mrs. Ayrton, his observations agree with our own.

SUMMARY.

Conditions have been found under which steady arcs can be maintained with currents from 120 to 700 amp. and voltages from 15 to 60 v.

The appearance of steady arcs and of the various unsteady arcs that were encountered are described.

A technique for accurately determining the relation between current, voltage and the length of carbon arcs has been developed, and led to results which are given tabular form.

These results lead to the conclusion that $e = 0.99\ L$, where $e =$ voltage over the arc, $L =$ length in millimeters from the tip of the cathode to the bottom of the anode crater. This substantiates the conclusions of the previous paper[3] and is in accordance with the results obtained by Watts.[6]

This research was carried out in the Department of Electrochemistry, University of Toronto, during the winter of 1922-23. The writers are indebted to Dr. W. Lash Miller for the interest he has shown in the work.

DISCUSSION.*

A. H. Heatley[1]: It is interesting to note that the ratio between the length and voltage measured over the whole arc (Tables I to V) checks with the ratio between a small change in length and the corresponding change in voltage (Tables VI to VIII). This indicates that in this arc the potential drops at the anode and cathode are practically zero.

A Member: On page 144, I see that the authors are careful not to mention fused carbon. I want to give a little sketch of something that happened to us not long ago. We had a Hoskins plate furnace in operation, which had a firebrick back, in front of which was placed a graphite plate and then a series of carbon

* In the absence of the authors the above paper was presented by Colin G. Fink.

[1] Niagara Electrochemical Co., Niagara Falls, N. Y.

plates. Through some accident, the upper part of the contact between the carbon plate and the graphite plate became loose and as a result we had an arc around 2,000 amp., at 20 v. When we took out the first sheet of carbon, it showed signs of having been drawn in at the center. I will leave that for you to consider in regard to the question of fused carbon.

H. M. St. John[2]: It seems to me that in order for this research to be complete it would be necessary to carry out a similar line of experiments with other electrodes, viz., electrodes containing different amounts of ash and possibly of different physical character.

The authors refer to the fact that when they used powdered silica it made a pronounced difference in the voltage of the arc, consequently in the length of the arc at constant voltage. As a matter of fact, a comparatively small variation in the ash of those carbons, which I believe is stated as 0.1 per cent., would make quite a difference in the arc length at any given voltage. This is true not only of the ash, but also of the various physical characteristics of the carbon, which determine what you might call its volatility. If the electrodes had been made of artificial graphite, the results would have been different. If they had been made of raw lamp black, the results would also have been different. The results would vary according to whether coal tar or pitch were used in the binder, and also according to the temperature maximum at which the electrodes were baked, and the rate at which they were baked during the carbonization period.

It does not seem at all surprising that there was a substantial variation between the results obtained by the authors and those obtained by Mrs. Ayrton and others. The experiment, while it was admirably carried out so far as attention to detail is concerned, certainly does not justify anything in the way of sweeping conclusions except that, under certain given conditions, the voltage of an arc varies with the arc length. This has been well known for some little time. Similar experiments carried out with a variation in the quality of the electrodes might point the way to some more valuable information.

J. Kelleher[3]: In the authors' paper, page 142, they mention

[2] Detroit Lubrication Co., Detroit, Mich.
[3] FitzGerald Labs., Niagara Falls, N. Y.

under the caption of "steady arcs": "Any unsteadiness in the divmeter readings was invariably accompanied by quite noticeable fogginess in the crater, through which the hole could not be seen." Would that not indicate that the authors, in their experiments on the length of the arc with regard to the voltage, were approaching a high intensity arc?

PRESTON R. BASSETT[4]: The electrodes with which Westman and Clapson worked were not impregnated with any chemical compound other than carbon, as I understand it, and it would therefore be impossible to obtain an actual opaque vapor in the crater; but I have noticed in very deep craters with cored carbons, that this fogginess is apparently the dimming of the crater at the bottom in the deepest part. That is, the bottom of the crater does not carry its share of current to the arc and, therefore, loses in brightness and falls down perhaps to only one-quarter in intrinsic brilliancy which the outer rim of the crater still maintains. I took that to be what the authors referred to as the fogginess in the crater; that is, losing of light, rather than an increase of light.

A. E. R. WESTMAN (*Communicated*): Referring to Mr. St. John's remarks, Run 44 (Table IV, page 147) shows that there is not much difference between graphite and carbon electrodes.

The weight of silica vaporized from the electrodes per minute, by an arc of 700 amp., calculated from the ash content of the electrodes, is only one milligram, while about one gram of powdered silica per minute must be thrown into the crater to keep the voltage abnormally low. No doubt it would have been better to use electrodes of chemically pure carbon, but we did not have any.

What we called "fogginess" was a brilliantly luminous mist through which the bottom of the crater could not be distinguished. This was observed only when the voltage was unsteady. With a steady voltage the small hole drilled in the center of the crater was "black and distinct in outline" (page 142). Mr. Bassett's explanation does not seem to fit.

[4] Research Lab., Sperry Gyroscope Co., Brooklyn, N. Y.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE ELECTROCHEMISTRY OF THE HIGH INTENSITY ARC.[1]

By Preston R. Bassett.[2]

Abstract.

The high intensity arc is a distinct type of electric arc. Consideration is given to the progressive changes in phenomena of various types of arcs with increasing current. Carbon arcs and ordinary flame arcs change their behavior fundamentally with large currents. The tendency to produce two arc flames, a positive and a negative, is present in an obscure form in practically all arcs. In the high intensity arc, this phenomenon has been enhanced to a point where the two flames are separate and distinct, and each flame performs a separate function. The high intrinsic brilliancies obtainable with this type of arc are discussed, and the carbide flame has been suggested as an explanation for the abnormal brilliancies produced.

INTRODUCTION.

The high intensity arc is a new type of electric arc, which has been developed and put into extensive use during the past ten years. A. Blondel[3] in France, whose elaborate researches in the field of the electric arc have become classic, was the first to note and record the positive flame effect at high currents in mineralized carbons. He did not, however, follow up these interesting observations, as he probably did not appreciate the great possibilities of the new and transitory phenomenon which he glimpsed. Beck[4] in Germany some time later attempted to produce this type of arc by surrounding the burning electrodes with an inert gas

[1] Manuscript received June 27, 1923.

[2] Research Lab., Sperry Gyroscope Co., Brooklyn, N. Y.

[3] Recent Progress in Flame Arc Lamps, Andre Blondel, Bulletin de la societe International des Electriciens.

[4] Searchlights, C. S. McDowell, Trans. Am. Inst. Elec. Eng. (1915).

such as alcohol vapor, but his method has been found impractical and is now obsolete. It is to Elmer A. Sperry, one of the electric arc pioneers of this country, that the credit is due for the successful development of the high intensity arc in its present commercial form.

The work has been carried much further in this country than elsewhere and the light has been successfully applied in a number of different fields. The fact that it has been found impracticable to operate this arc at less than fifty amperes or in units of less than 20,000 c. p. has confined its utilization to special fields.

The arc was developed during the first years of the war for use in searchlights. It is the most ideal source for searchlights yet discovered, since its outstanding properties are tremendous brilliancy and extreme concentration approaching the point source. In one step the efficiency of the searchlight was increased 500 per cent by this new source, and it became one of the most effective weapons against night air raiding.

Considerable literature has accumulated concerning the light characteristics and various applications of the high intensity arc, a bibliography of which is appended. There has not been published to date, however, any paper dealing in detail with the physical and chemical theory of this arc. The present paper is the first attempt at a complete explanation of the phenomena involved.

An electric arc may be maintained between any two electrical conductors, hence there are almost unlimited methods of classifying arcs. Perhaps the most practical general classification is to divide them into arcs between carbonaceous electrodes and arcs between non-carbonaceous electrodes. It may seem strange to have the main classification hinge about one element, but this element, carbon, is so ideally suited for arc work that carbon base electrodes have always been and still are of more practical importance than all others combined.

The unique property which places carbon in this position is that it has no melting point at atmospheric pressure, but has a volatilizing or subliming point which is higher than the melting point of any element or compound. This means high temperature without molten material or in other words a clean arc. With

carbon as the basis of the electrode almost any material may be introduced into the arc by being mixed with the carbon either in whole or in part, as in cored carbons.

In modern electrode manufacture, the introduction of compounds into the carbons for specific purposes has become quite general. The following are the main purposes for impregnating carbon electrodes.

1. Increasing the luminous efficiency.
2. Producing arcs of special color or spectrum characteristics.
3. Decreasing the arc voltage.
4. Centering the arc crater on the electrode tip.
5. Allowing steady operation with longer arcs.
6. Reducing noise, hissing on d. c., humming on a. c.

To the above list of uses of auxiliary materials in carbon electrodes, the high intensity arc has added

7. The production of very deep anode craters.
8. The creation of a flame of high intrinsic brilliancy confined within the deep crater.
9. Giving a directive force to the negative arc flame.

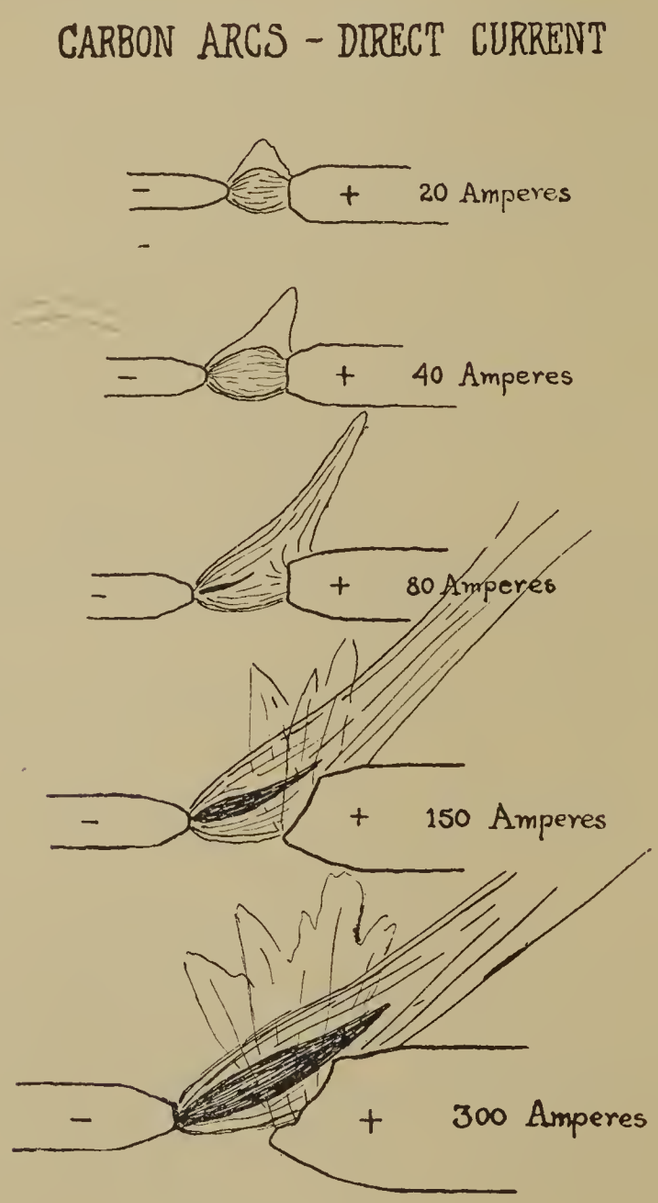
THE CARBON ARC AND AMPERAGE.

In order to understand the action of the high intensity arc it is essential first to study the effect of amperage on the ordinary carbon arc. It is surprising that practically all literature on the arc has failed to mention the alteration of the type of arc discharge with change of amperage. This omission is due mainly to two reasons: first, most arc researches have been confined to low currents, probably by lack of laboratory facilities. The standard work on the electric arc by Mrs. Ayrton[5] is confined entirely to arcs of less than 30 amp. Another handicap to much of the previous arc work is that the vertical arc has been almost universally used in investigations.

The vertical arc, with positive upper and negative lower, masks many important phenomena, since the ascending air currents act in the same direction as the negative ions and gravity acts in the same direction as the positive ions. These extraneous forces com-

[5] The Electric Arc, Bertha Ayrton.

plicate and sometimes conceal the actual arc behavior. In the experiments here described, the horizontal arc was early adopted, since the four main forces all act on the arc in different directions and the effects of each are easily separable. Air currents act upward, gravity downward, positive ions to the right and negative charges to the left.



— Figure 1 —

Fig. 1 shows a series of arcs between ordinary carbon electrodes. In each succeeding sketch of the series the current is doubled. The progressive change of phenomena is evident. The 20 amp. arc is the familiar quiet little arc, having the usual small yellowish flame tip above the violet arc flame. The peak of the flame

tip occurs about half way between the positive and negative electrodes. Doubling the current shows the violet arc flame almost unchanged, but the tail flame has increased in length and has shifted toward the positive electrode. Doubling again to 80 amp. causes the tail flame to lean back over the positive electrode, so that its tip is no longer over the arc. It also increases in length to 4 or 5 in. The arc is now apparently issuing almost entirely from the negative electrode.

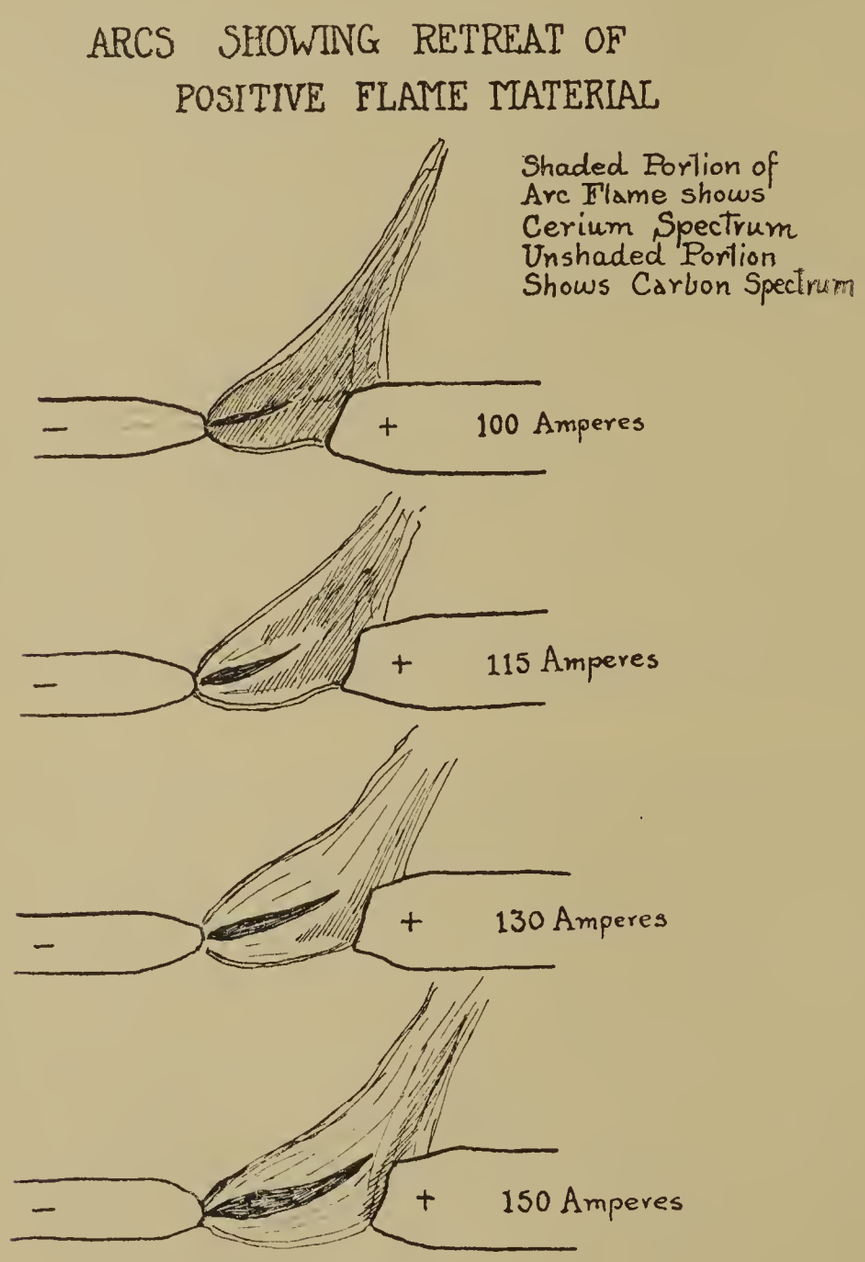
The next step 150 amp. makes this very evident. The arc flame has now become a high velocity jet from the negative, which strikes directly against the positive crater. The last step 300 amp. or over, exaggerates this negative blast condition to a point where the arc may be called unmanageable in practice. The negative flame now acts on the positive electrode with a scouring effect, similar to placer mining. The crater is gouged out unevenly, and unless elaborate precautions are taken the arc soon breaks into a roaring, shrieking arc due to access of oxygen to the uneven crater, and also to the rapid thrashing around of the negative flame in an endeavor to cover a crater larger than its own cross-section.

Another important change in the arc discharge with increasing current is the shift from the familiar carbon vapor, violet colored, discharge to the enhanced brilliant white negative tongue discharge. The first appearance of the negative tongue usually occurs quite suddenly at about 80 amp., as a thin white central thread in the negative flame. As the current increases above this point, the cross-section of the negative arc flame remains almost constant but the negative tongue swells in diameter and length. At a current of 600 amp. the negative tongue fills practically the whole negative flame and the familiar violet arc flame is confined to a thin sheath surrounding it. This tongue has seldom received mention in arc literature. Rasch[6] mentions it as an electron stream in referring to an experiment of Siemens.

The cause of the non-expansion of the cross-section of the negative flame with increasing current is undoubtedly the "pinch effect" in the conducting vapors. The self-induced magnetic effect, due to these high currents carried by the arc flame, concentrates it to a current density which may be the cause of the change

[6] Electric Arc Phenomena, E. Rasch.

of type of discharge. The tongue is always sharply separated from the violet arc flame, and has a distinctive spectrum disclosing many lines hitherto unknown in arc spectra.[7] This subject is now under further investigation by Dr. Louis Bell and the author.



— Figure 2 —

In the 20 and 40 amp. arcs, the flow of material from each electrode is intermingled and passes across the entire arc gap in both directions. It is the plating over of the positive material onto the negative tip which causes the well known graphite cap or (in exaggerated form) the "mushroom" on the negative. In arcs of

[7] Helium in the Electric Arc, L. Bell and P. R. Bassett, Popular Astronomy, 1923.

130 amp. and higher material no longer passes from positive to negative, hence the negative tip is always clean no matter what impurities may be in the positive. The increased velocity of the negative flame makes it impossible for ions to travel against it.

Arcs from 80 to 150 amp. show the transition stage from the commingled two direction discharge to the single direction discharge. Fig. 2 demonstrates the backing out of the positive ions. The positive electrode in this series is charged with a small amount of some compound which will color the arc flame, in this case cerium fluoride. These arcs are from original tracings made by lens projection of a magnified arc image on a screen.

All of the foregoing arcs consist of two separate discharges, the positive flame and the negative flame, but ordinarily these are not apparent as entities. In the low current arc they are intermingled and inseparable. In the high current arcs, the positive flame is practically obliterated by the overpowering negative blast. But under special conditions their presence can always be demonstrated.

Fig. 3 is a photograph of an arc on the instant of breaking. It shows the individual flames distinctly. Even 10 and 20 amp. arcs show the separate flames when the arc length is excessive and the arc voltage high. Blondel[3] noticed the two flames in his arc work and speaks of them as two plumes.

FLAME ARCS.

The ordinary flaming arc has been so thoroughly dealt with by W. R. Mott in several papers[8] before this Society that only a general summary of its characteristics need be given. The introduction of flame materials into the arc by means of an impregnated core in the positive electrode has been common practice since Bremer's original flaming arc lamps. The compound or salt gives in the arc two spectra, one in the arc flame proper, which is a line spectrum of the metallic component, and one in the shell or outside edge of the arc flame, which is the band spectrum of the recombined ions of the original salt or of the metal radical with oxygen. Almost all salts give these two spectra to some degree, but only a limited number give sufficient luminous efficiency to be

[8] Arc Images in Chemical Analysis, Trans. Am. Elcetrochem. Soc., **37**, 665 (1920). Chemistry of Flaming Arcs, Trans. Am. Electrochem. Soc. **31**, 365 (1917).

utilized. No single element or compound is used which gives efficiency in both the shell and core spectra. Calcium and strontium fluorides are used for the brilliancy of their recombining shell spectra. Cerium and other rare earths and iron are used for the brilliancy of their line spectra in the flame core.

All true flame arcs must operate at currents below 100 amp., since they depend for their light on the passage of the metallic ions from the anode to the cathode, which causes the whole arc flame to emit the distinctive spectra. In practice, flaming arcs have

Fig. 3.

always been operated at currents of less than 50 amp., and flaming arc literature has been confined to the low current arcs. Flame carbons at high current had always been considered erratic and properly so, since they no longer behaved according to precedent. A calcium fluoride electrode at 150 amp. does not color the arc flame between the electrodes, but produces a very long yellow tail flame of low intrinsic brilliancy extending over 31 cm. (12 in.) in length above the anode. Other materials behave in a somewhat similar manner. Cerium, however, does not produce an excessive tail flame, but shows a tendency to create momentarily a brilliant flame immediately at the positive crater. This rudimentary

positive flame has been fostered and improved until the new and distinct type of arc, called "the high intensity arc" has been evolved. The development called for much that was new in all branches of the field. Research in the production of proper electrodes, in precision carbon positioning for proper burning and designing, completely new systems of arc control mechanisms, were all essential to the success of this development.

The high intensity arc is the first arc in which both the positive and negative flames have been utilized as separate entities and for

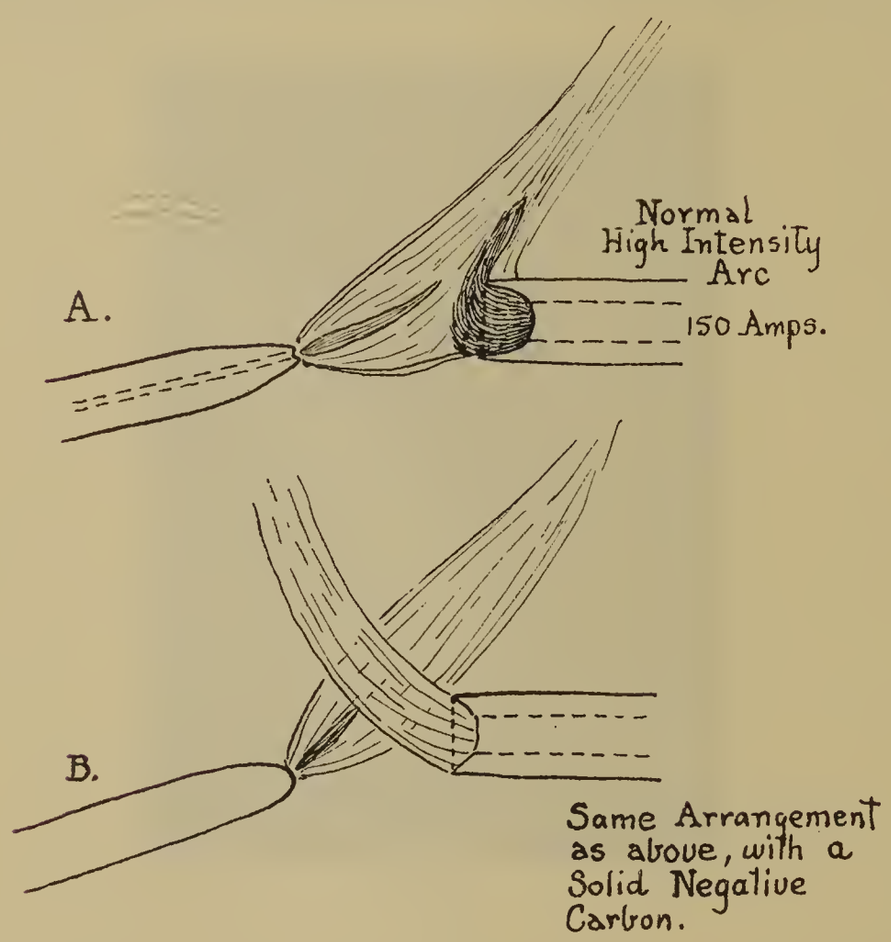
Fig. 4

different purposes. The positive flame emanating from the core of the positive electrode is the light producer, the negative flame comparatively non-luminous is the arc maintainer, bridging the gap between the electrodes. The negative flame is also used to confine the positive flame within the positive crater. Fig. 4 is a photograph of the 150 amp. high intensity arc. It will be noticed that the negative electrode is set at an angle to the positive, so that the negative flame sweeps upward across the mouth of the positive crater, confining the brilliant positive flame to the crater but carrying off the overflow steadily in a continuous direction. Unfortunately the great differences in brilliancy of different portions

of the arc makes it difficult to photograph all the parts clearly, hence a better idea may be obtained by referring to Fig. 5 (A) showing a cross section diagram of the arc.

Taking the 150 amp. high intensity arc as a standard, since it is the one most used, its structure and behavior will be analyzed in

EFFECT OF DIRECTIVE CORE
IN NEGATIVE ELECTRODE



— Figure 5. —

detail. The positive is 16 mm. in diameter and contains a core of 8 mm. diameter. All of the flame material is incorporated in this core, the shell being of the purest carbon obtainable with a minimum percentage of ash. The negative carbon is 11 mm. in diameter, and contains a small 3 mm. soft carbon or neutral core. A neutral core is one which contains arc supporting but not light

emitting materials. The negative carbon is set at an angle of about 15° below the axis of the positive. The positive carbon is slowly rotated.

When the arc is burned under these conditions, it appears as in Fig. 4 and 5 (A). The positive carbon forms a deep uniform crater, which is of nearly the same diameter as the electrode. Both of these conditions, deep crater and crater diameter equal to the electrode diameter, are characteristic of the high intensity arc and are produced and maintained in the following way.

The core containing the flame material becomes an excellent conductor at high temperatures and, therefore, almost all of the current enters the arc through the positive electrode core. Since the core burns away rapidly due to the high current density the shell remains as a wall, which thus forms the deep crater. The electrode is consumed at a rate which is so rapid that the oxygen of the surrounding air has little opportunity of causing the electrode to spindle or taper on the outside.

By means of shrouding the electrode from the air up to within an inch of the crater and running at this abnormal current density, the crater diameter is kept very close to the electrode diameter. The continuous rotation of the arc keeps this crater wall uniform. The shell burns away to a sharp lip with concave inner walls, making almost a perfect hemispherical cavity. This uniform crater is essential to the high intensity arc, since it acts as the container for the brilliant positive flame. The percentage of flame material in the core, the current density and the shell and core ratio are so adjusted that the supply of the positive vapor is at all times sufficient to fill to overflowing this positive crater. The flame, in fact, bulges out in front of the crater and is only confined by the continuous pressure of the negative flame against it. The establishment of a considerable pressure exerted by the negative flame against the positive vapor is a large factor in the production of the increased brilliancy of the positive flame.

The continuous opposing forces exerted against each other by these two flames have a tendency to cause the flames to push each other aside, so that both may pass by each other without pressure. Any ordinary solid negative electrode will immediately give an unsteady crossed flame type of arc as shown in Fig. 5 (B). Such

an arc condition gives less than 50 per cent of the candle power of the normal high intensity arc. To prevent this condition it has been necessary to utilize a core in the negative electrode for the new purpose of giving the negative flame such a directive force that it cannot be pushed aside by the counter-pressure of the positive vapor. The 3 mm. soft core in the negative carbon makes a seat on which the negative flame tends to rest and from which it is only displaced with great difficulty. In the ordinary types of arc, this use of a negative core has not been necessary, since in no other arc is there a strong pressure tending to divert the negative flame from the positive crater.

THE VOLTAGE DISTRIBUTION IN THE ARC.

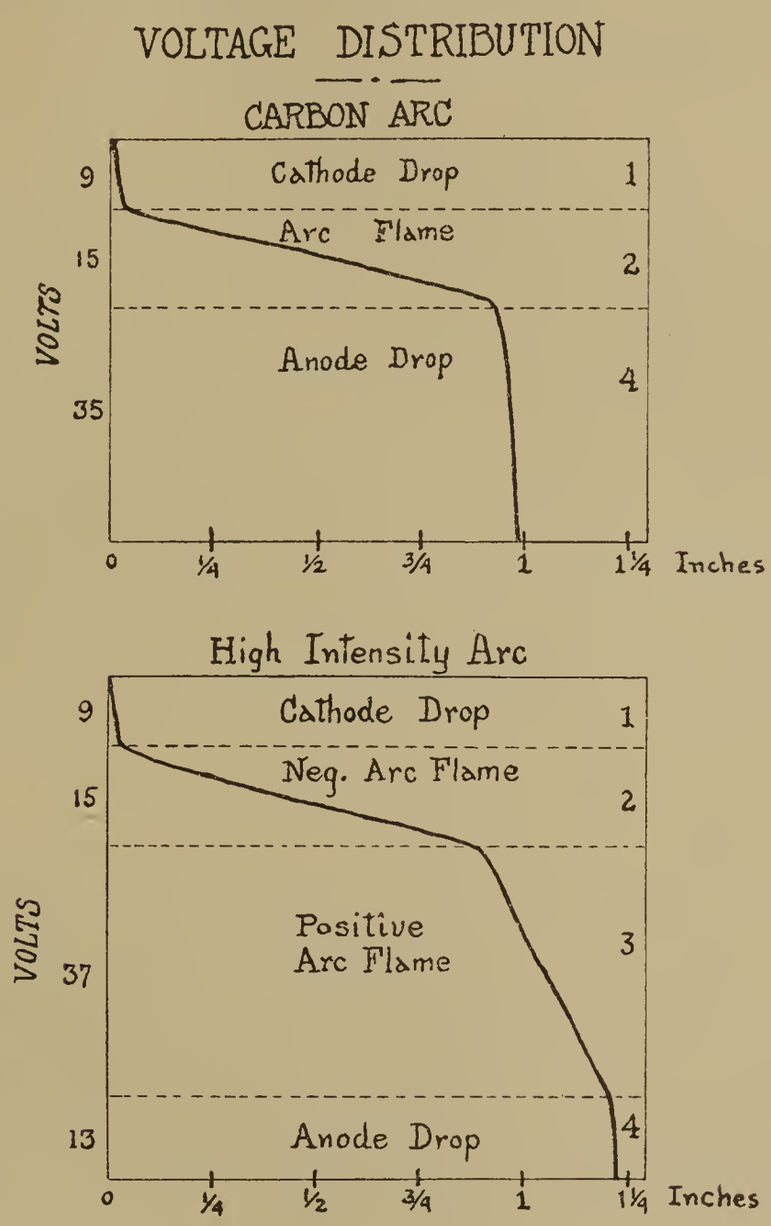
There is considerable energy consumed at all arcs, and the consequent fall of potential across the arc has been investigated many times perhaps most thoroughly by Mrs. Ayrton.[5] The fall in voltage across the arc is divided into three parts, the cathode drop, the drop through the arc flame, and the anode drop. The anode drop and the cathode drop are fairly constant for a given electrode material, regardless of the length of arc. The drop through the arc flame is directly dependent on the arc length. In the case of carbon the cathode drop is 9 v. and the anode drop is 35 v. See Fig. 6.

The presence of flame materials in the positive carbon reduces the arc voltage. This reduction takes place for the most part as a reduction of the anode drop, but the flame materials in the all-luminous arc also cause a gentler potential gradient through the arc flame.

In the new type of separate flame arc the distribution of voltage was determined by means of slender carbon exploring rods. This investigation proved of considerable interest, in showing the large percentage of the arc energy consumed in the positive flame and crater. The curve for this arc running under good conditions is shown in Fig. 6.

The cathode drop is 9 v., the same as in the pure carbon arc. The fall through the negative flame is the normal gradient up to the point of contact with the positive flame. At the junction of the positive and negative flames there is a considerable fall of voltage, and through the rest of the positive flame the voltage

gradient is much steeper than through the negative flame. It was impossible to determine the actual anode drop since an exploring rod could not be thrust into the crater without distorting or extinguishing the arc.



— Figure 6. —

The main point to be noticed is that only 24 v. or 37 per cent of the arc voltage is consumed from the negative carbon across the entire arc length to the positive flame. The remaining 63 per cent of the voltage is consumed through the positive flame in the crater including the anode drop. This shows the tremendous amount of energy expended within the crater. When the current density is also taken into account the energy density

proves to be 3.6 times the energy density of a pure carbon positive crater. The 150 amp. arc converts continuously 7.5 kw. of electrical energy into radiant energy in the small space of a half inch hemispherical cup. This gives a maximum candle power of 130,000 and an actual luminous efficiency of 15 per cent of the total radiation.

THE POSITIVE FLAME.

During our investigations on this arc, many peculiarities of the positive flame have been noticed which could not be explained by any existing arc theories. The published explanations of the high intensity arc up to the present have considered it to be an intensified flaming arc, the extra brilliancy being due to the concentrated ionized cerium vapor in the crater, superimposing its thousands of spectrum lines on the continuous spectrum of the carbon crater walls. But this explanation has always left much to be desired. The relative opaqueness of the positive flame in completely obliterating the crater bottom in about 9 mm. depth is hard to reconcile with a pure line spectrum. No usual form of arc discharge has any apparent opaqueness, even when viewed through a depth of over an inch.

Another point of difference, not compatible with an entirely ionized or vaporized arc, is the fact that under certain conditions the positive flame gives off quantities of black soot. The soot from the arc always comes off in large fluffy flakes which settle slowly from the air. Under a microscope 440 magnification shows these flakes to be crumpled up membranes of pure carbon of no detectable thickness and almost transparent when a single layer is viewed. The membrane appears to be of uniform lacy appearance. This new product should be called electric lamp-black or arc lamp-black, as it is similar in method of formation to the other lamp-blacks. No extensive tests have been made of its properties. A pure carbon arc cannot be forced to soot, no matter how much the current density is increased.

A third property of the high intensity flame which gives a clue is its remarkable white spectrum. Spectrophotometric and bolometric data show energy curves that are not unsimilar to black body radiation curves, after the line spectrum irregularities have

been smoothed out. The flame gives a very brilliant continuous spectrum, which has, however, been overlooked on account of the beauty and brilliance of the many-lined cerium spectrum also present.

THE CARBIDE THEORY.

The above considerations have led to a new theory of the high intensity arc, which is of interest in that it places this arc as the first of a new class of illuminants, and withdraws it from the class of "flaming arcs" proper.

As already described, the positive electrode consists of a core of cerium fluoride and carbon, and the shell consists of a non-graphitizable pure carbon, such as produced from a lamp black base. As the positive is consumed, the temperature of the core material is raised as it approaches the crater. At a distance of about 5 mm. (3/16 in.) back from the burning core face, the temperature reaches a point where the dense core is softened and made somewhat spongy by the fusing of the CeF_3. When within 0.8 mm. (1/32 in.) of the core face, the temperature has reached 3500° and the CeF_3 reacts with the carbon,

$$CeF_3 + 2C \leftrightarrows CeC_2 + 3F$$

This reaction is reversible in this region, and causes the formation of a layer of almost pure graphite on the core face, by the redeposition of carbon from the carbide in accordance with Dr. Acheson's theory, and also Moissan's experiments[9].

Since the current density and vapor pressure in the crater are too high to allow the complete ionization of the CeC_2, and since CeC_2 is stable at extremely high temperatures, it is given off from the core face in the form of minute, highly incandescent particles. The density and temperature conditions in the crater are such that the following reaction takes place in the crater flame,

$$CeC_2 \leftrightarrows Ce + C_2 \text{ or } 2C^{ion}$$

This reaction is also probably reversible, or an equilibrium equation.

The abnormal density in the crater establishes an equilibrium

[9] Electric Furnace, H. Moissan.

between the ionized elements and the carbide. If the density is decreased, either by lowering the current or allowing the positive flame to pour out unimpinged by the negative, the equilibrium changes and more carbide is ionized whereas little recombines, the spectrum rapidly falls back to the cerium line spectrum, and the intrinsic brilliancy drops more than 50 per cent.

If the positive flame is carried away normally in the tail flame the carbide is completely ionized shortly after leaving the crater, and then the ions recombine in the tip of the tail flame as in the shell of the ordinary flame arc.

$$O_2 + Ce^{ion} + 3F^{ion} + C^{ion} = CeF_3 + CO_2$$

The CeF_3 makes a white fume which is a combustion product of all white flame arcs. If the positive flame does not normally pass off through the tail flame, but is forced out into the air before being completely ionized, the cerium carbide burns incompletely as follows:

$$CeC_2 + O_2 = CeO_2 + C_2$$

This is always the condition when soot is produced. The soot is similar to that cast off by many organic substances when burned.

The analogy is very close. In organic substances the heaviest soot producers are those where carbon atoms are linked to each other in the original molecule, preferably by two or three valence bonds, that is, unsaturated organic compounds. Cerium carbide might be called unsaturated, since its formula, CeC_2, calls for a double valence bond between the two carbon atoms; hence when the oxygen removes the cerium, linked carbon atoms remain, producing a heavy lamp black. The formation of the thin lacy membrane can be explained as the actual contact surface of the carbide flame with the air. This contact surface consists of minute liquid particles of carbide, which when suddenly robbed of the cerium leave a carbon membrane skeleton of the contact surface. Complete cones of this soot have been identified, appearing as though they had been lifted off of the tip of a flame.

TEMPERATURE AND INTRINSIC BRILLIANCY.

It was thought for a long time that carbon at its volatilizing point of 3700° C. gave the maximum brightness that could be obtained from incandescence or pure temperature radiation. This is about 180 c. p. per sq. mm. Moissan's classical work on the electric furnace[8] opened up a new class of compounds, the carbides, which he studied in some detail. He prepared cerium carbide and records its melting point as below 3500° C.

He mentions also the fact that it is readily decomposed by water, giving acetylene and some methane. In our early experiments with high intensity electrodes, craters were frequently encountered from which the carbide had not been completely volatilized when the arc was extinguished, and a strong smell of acetylene was given off on the addition of a drop of water to the crater. In the perfected electrode there is no trace of carbide in the crater, as it is all volatilized or else reformed into fluoride, leaving only a clean graphite core face.

Moissan does not mention the boiling point of CeC_2, and no definite determination of this figure has been made. From W. R. Mott's experiments on relative volatilities of refractories[10] the boiling point can be estimated to be in the neighborhood of 4700° C.

With an incandescing flame of this temperature, 1000° higher than the carbon arc crater, excessive brilliancies are attainable, since the total radiation increases as the 4th power of the absolute temperature and the visible radiation as about the 6th power.

The high intensity arc for any given set of conditions runs very uniform in intrinsic brilliancy, but by forcing the current density so that excessively deep craters are formed and a long column of the vapor is produced in the crater, brilliancies have been obtained as high as 1400 c. p. per sq. mm., or 8 times the brilliancy of the carbon arc crater. Such arcs are not practical due to the rapid rate of consumption of the electrodes.

Many attempts have been made to determine the temperature in the high intensity crater with a large divergence of results. The Bureau of Standards[11] obtained a figure of 6000° K. by

[10] Relative Volatilities of Refractory Materials, Am. Electrochem. Soc. 34, 255 (1918)

[11] Spectral Composition of High Intensity Arcs. Bureau of Standards Technological Paper No. 168 (1920).

the rotary dispersion colorimeter. The method is inaccurate for a source of this type, due to the selective cerium line spectrum, which is greatest in the blue and violet and hence shifts the resulting hue toward the blue, resulting in a temperature figure which is too high.

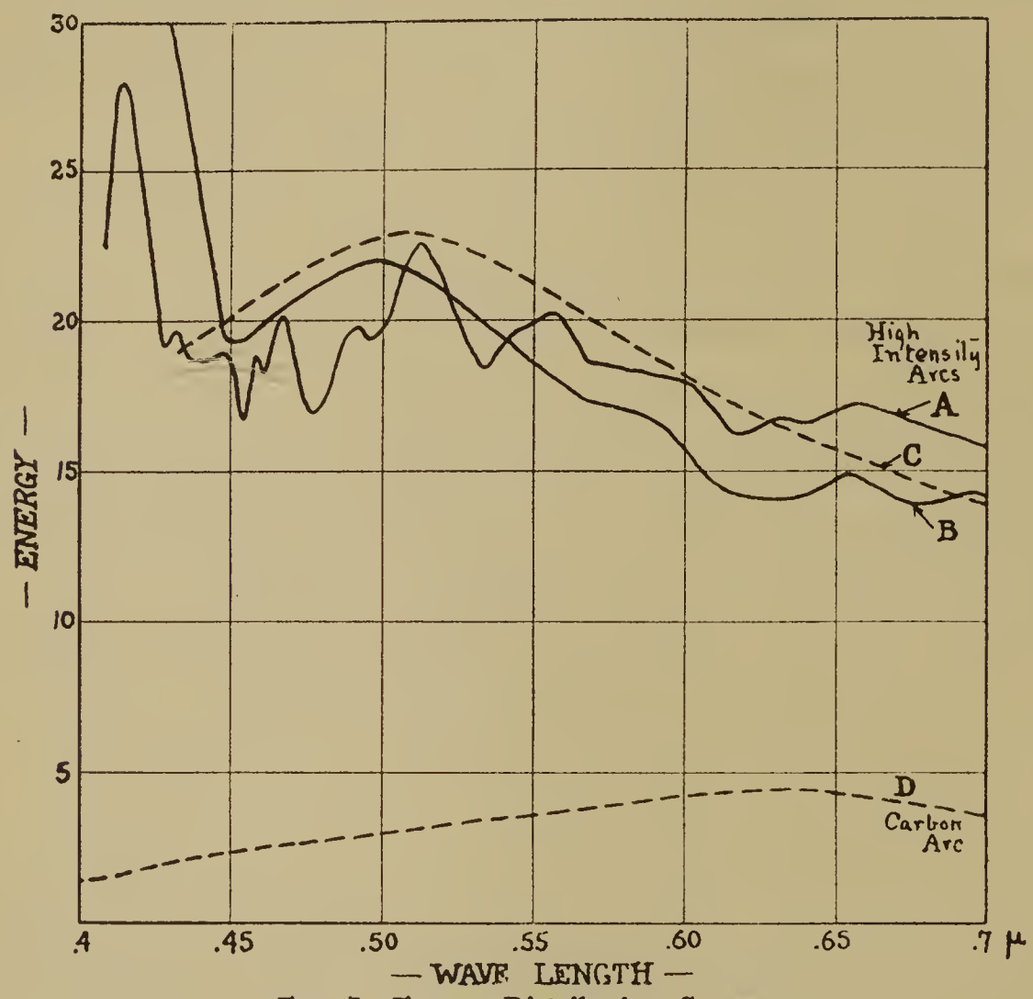


FIG. 7. Energy Distribution Curves.

Dr. C. G. Abbott's bolometer curve C in Fig. 7 is approximately a correct black body curve for a temperature of about 5000° C. This is a good check on the boiling point figure 4700° C. of cerium carbide. Curves A and B of Fig. 7 give typical spectrophotometric energy distributions of the same arc. The spectrophotometric curves show the complex nature of the spectrum, but still show a tendency toward a maximum energy point corresponding to Dr. Abbott's curve. The great increase in energy, below 0.43 μ, is quite characteristic of the high intensity arc, but is probably due to the cerium line spectrum, which is most intense in this region rather than to the carbide black body spectrum.

With the data available at present, therefore, the best estimate of the temperature of the high intensity arc is about 4700° C., or 5000° absolute, but its intrinsic brilliancy, bluish hue, and abnormal actinic light are all greater than would be produced by black body radiation of this temperature, and are due to the intense cerium line spectrum which is superimposed on the carbide spectrum.

TABLE I.

Intrinsic Brilliancy of Well Known Illuminants.

Intrinsic Brilliancy; c. p. per sq. mm.	Luminescence Line and Band Spectra	Solid Incandescence Continuous Spectra	Flame Incandescence Continuous Spectra
0.0001-0.001	Bunsen Burner	Nichrome Res. Unit	Pine Knot Flame
0.001-0.01	Moore Tube, CO_2	Iron at its Melting Point	Candle Flame
0.01-0.1	Mercury Vapor Arc	Welsbach Mantle	Kerosene Flame
0.1-1.0	Carbon Arc Flame	Carbon Filament Lamp	Acetylene Flame
1.0-10.	Flaming Arcs	Tungsten Filament Lamp	.....
10-100	.....	Gas-Filled Incandescent Lamp	.....
100-200	.....	Carbon Arc Crater	.....
500-1000	.....	.....	High Intensity Arc
Sun at Zenith 920			
1000-1500	.....	.....	High Intensity Arc Forced

Table I is a chart of intrinsic brilliancies of well known illuminants. It has been prepared to show the range of brilliancies attained by the three usual methods of producing light—luminescence, solid incandescence and flame incandescence. Flame incandescence has furnished man with all of his light from palaeolithic times until the last few generations. Electricity in

a remarkably short time converted illumination almost entirely to solid incandescence and luminescence. True flame incandescence was actually deserted by electricity. Now, however, electricity and the incandescent flame have joined hands and produced a unique illuminant, the most brilliant yet known and a worthy beginning of a new chapter in electric illumination.

ACKNOWLEDGMENTS.

The author wishes to acknowledge his indebtedness to W. R. Mott for his helpful suggestions and criticisms of this paper, and to the National Carbon Company for their excellent co-operation in producing many special electrodes for us during the development period. My thanks are also extended to Elmer A. Sperry, through whose untiring interest and guidance these investigations were made possible.

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DISCUSSION.

J. Kelleher[1]: Can Mr. Bassett explain the phenomenon of the double arcs observed in a small electric furnace. I wrote a paper

* Other than that referred to in the footnotes.

[1] c/o FitzGerald Labs., Niagara Falls, N. Y.

on this in 1920. The bath arced; it consisted of cast iron containing nickel. I had a great deal of trouble in holding the arc at a voltage of 74 v. and a current of 300 to 400 amp. The arc was blown out by another one starting from beneath the bath's surface. Is there any relation between this and the high intensity arc?

PRESTON R. BASSETT: Under special conditions you can obtain interesting double arcs with metal electrodes. With iron and copper, I have obtained double arcs where the flames would brush past each other, one from one electrode and the other from a second. As long as they were in contact at some point, the arc would stay lit. Sometimes the flames would whirl around and make a musical arc. The speed of whirling would be the pitch of the musical tone it gave out. It is all part of this two-flame phenomenon. I have noticed the fact that there is usually a flow of material from both electrodes. It is only in unusual cases that the two flows cause separate flames, such as in the arcs you found in your furnace and in the high intensity arc. Usually they are entirely masked either by intermingling or one flame being obliterated by the other.

J. KELLEHER: How does Mr. Westman's formula, as given on page 149, "$e = 0.99\ L$" compare with the graph of the voltage distribution on the carbon arc given in your paper on page 165?

PRESTON R. BASSETT: I have not compared them accurately. In fact all of the arcs that I have measured have necessarily been at least three-quarters of an inch to one inch in length in order to obtain the two flames separate. All of the exploration has been carried on with an exploring electrode, or carbon needle, to obtain the voltage drop across different parts of the arc. There may be other ways of doing it that would give somewhat different cathode and anode drops.

J. KELLEHER: Mr. Westman's formula does not include the cathode and anode drop, and I was wondering if there was any error that you had observed in his method of determining the

formula "e = 0.99 L" after your work with the cathode and anode drop, which would introduce a constant into his formula.

PRESTON R. BASSETT: My figures agreed closely with the figures of Mrs. Ayrton in her book "The Electric Arc." I have never measured the cathode drop above 400 amp. It may be that, where the flame gets to be entirely a negative tongue discharge, the cathode drop may change.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE FIRST LOW VOLTAGE GAS FILAMENT LAMP.[1]

By D. McFarlan Moore.[2]

Abstract.

For many years all luminosity due to the action of electricity in gases was associated with high voltages. The light between the two terminal electrodes of a small Geissler tube, or of a tube lamp such as used in the Moore long tube system, is positive column light, which in a measure accounts for its much greater intensity and efficiency. Several years ago it was found that luminosity in gases could be produced solely by voltages as low as 110, but it was a negative glow light of low intensity that surrounded the metal electrodes in a bulb of rarified neon gas. Although the ice on the problem was broken by the negative glow lamps, there remained the far more difficult problem of obtaining positive column light on low voltages. This paper announces such lamps, and contains, also, a brief resumé of the history of gaseous conduction and its many contacts with electrochemistry.

Light without heat is still the dream of many physicists who have looked for it in the realm of gaseous conduction, the phenomena of which can roughly be divided into the luminous and non-luminous. Until comparatively recent years, practically all gaseous conduction phenomena were dependent upon the use of high potentials, in various forms and under various conditions. The announcement of the first low voltage gaseous conduction lamp[3] opened a field of new possibilities. However, its luminosity

[1] Manuscript received August 14, 1923.

[2] Edison Lamps Works, Harrison, N. Y.

[3] Gaseous Conduction Light from Low Voltage Circuits, Trans. Am. Inst. Elec. Eng. March 26, 1920.

was due to the negative glow or corona phenomena, which seems to be inherently inefficient. It has been questionable from a scientific standpoint whether or not it would ever be possible to obtain a positive column lamp which will start and run on potentials less than 220 v., but such a lamp is described in this paper.

The basic principles upon which it operates are such that hopes are entertained that it can be developed into a new and very useful light source. The steps leading up to this result have been interesting, and I have been requested to touch upon some of the high points in gaseous conduction lighting and keep in mind the various electrochemical problems involved.

Lightning and the glass globe of Hawksbee of 1750 were the first examples of electric lighting, and they were both dependent on gaseous conduction. Geissler invented his well known tube in 1858. Plucker supplied it with various gases, and in 1873 Crooks caused substances to fluoresce under cathode bombardment at very low pressures. Novel lamps somewhat of this character were produced by Tesla about 1891. Since then the development of gaseous conduction light centered at first on small bulbs, then, at various intervals, shifted to tubes varying from a few feet to 250 ft. in length (that required about 20,000 v.), and then back to bulbs of various sizes. This course resulted in the devising of a score of distinct types of gaseous conductor tubes and lamps.

The New York electrical show of 1896 exhibited the first "filamentless lamp" or small bulbs provided with metal spirals as electrodes, which were covered with negative glow light, and also tubes about 7 ft. long and 2 in. in diameter with large external electrodes at each end. They were lighted by an intermittent current, produced by vacuum vibrators. The color of the light was white due to the CO_2 that was produced from the residual organic matter, due to the bulbs and tubes being rinsed with commercial wood alcohol.

The "vacuum tubes" shown at the electrical show of 1898 were somewhat similar, but aubepine (a perfume oil) was substituted for the wood alcohol and a rotary vacuum break about the size of a milk bottle was the source of the special current attached to the tubes. This interrupter was also used as the first radio

"vacuum tube." That is, the pulsations emanating from it affected the distant coherer, and the external spark or discharge was eliminated for the first time. Later such lighting vacuum tubes were lighted by current produced by the first specially designed inductor generator, producing alternations of about one million per minute, and some of the tubes were also lengthened by building them *in situ*. Since the intensity of the light was much increased, rosolic acid was used within internal electrodes to furnish the CO_2 gas.

About this time various types of bulb lamps were also produced, the electrodes of which consisted of lime at high temperatures. Necessity for larger quantities of gas and under more perfect control resulted in the development of the automagnetic feed-valve, and the first gas to be automatically fed to tubes 1¾ in. in diameter and several hundred feet long and provided with internal carbon electrodes, was air. Many miles of this type of light-giving tubes were installed throughout the world. There was substituted for the air, however, various gases, notably nitrogen, which was first obtained from tanks and later from the atmosphere, by using phosphorus to absorb the oxygen. Just why it is necessary continually to feed gas to such a tube is a problem in electrochemistry, but the gas whether nitrogen or CO_2 is changed from its gaseous form to a solid product, and after a life of about 10,000 hr. the organic deposit within each graphite electrode is more than a handful. When nitrogen was fed from the atmosphere it was noted that argon gradually made itself prominent in the spectrum.

Tubes in various forms were also provided with feed valves and made up in portable units. When supplied with CO_2 they produced a light that today is considered the standard for accurate color matching. Large tube lighting units have their commercial limitations, however, whether built *in situ* or in portable form, so that once more the desire for a simple bulb form of electric gas lamp became acute, and the first low voltage gas lamp already referred to resulted. However, the possible candle-power on 110 v. from such neon corona lamps was meager, and, therefore, the commercial possibilities restricted.

Higher candle-powers were reached in another new type of

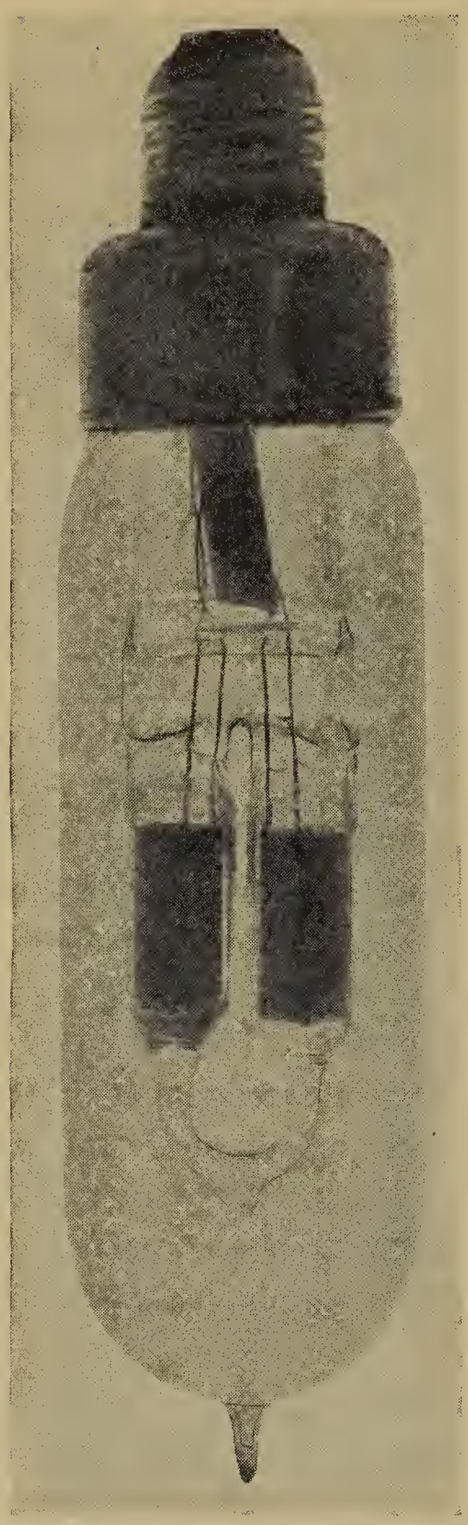

FIG. 1.
Moore low voltage positive column gaseous conductor lamp, 220 v.

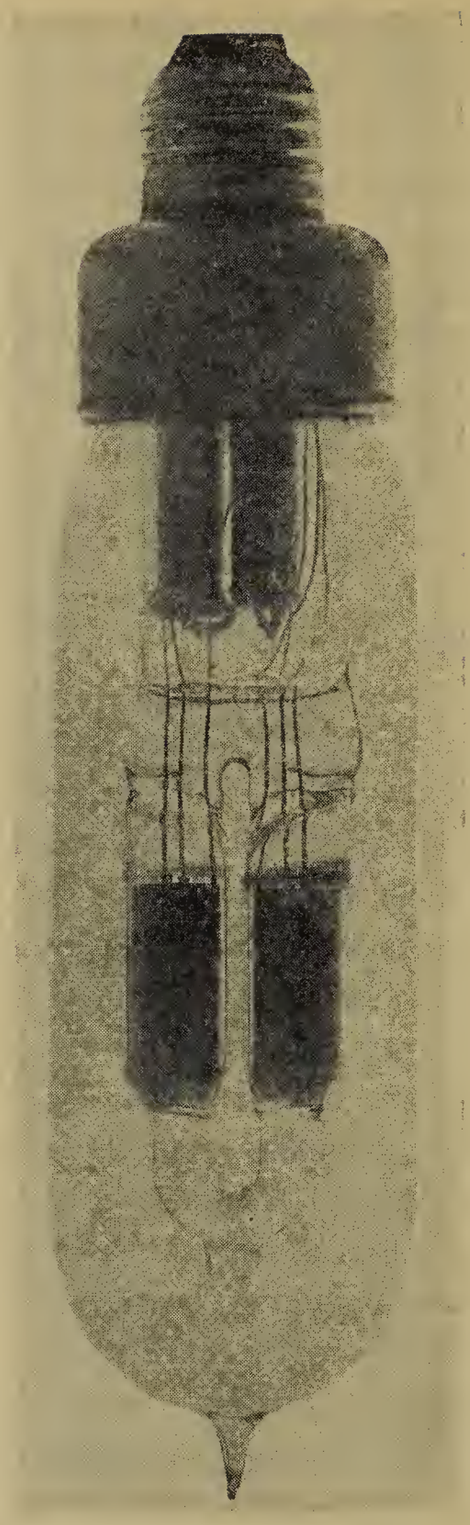

FIG. 3.
Moore low voltage positive column gaseous conductor lamp, 110 v.

low voltage lamp[4], in which the light emanated simultaneously from three sources: (1) the neon gas, (2) the tungsten arc, and (3) the more or less highly heated tungsten electrodes.

It was realized that if a positive column could be made by

[4] A low voltage self-starting Neon Tungsten arc incandescent lamp. Trans. Am. Inst. Elec. Eng. Sept. 26, 1921.

220 or 110 v. it would probably have long life due to the small tendency of a positive column to blacken, and also that it could be made bright and efficient. But with ordinary electrodes, of iron for example, 220 v. even in neon gas would not produce any positive column light, and therefore special expedients needed to be devised that were simple, that is, that did not involve the use of a high potential transformer or other auxiliary apparatus. Fig. 1 is a photograph of one of these new low voltage positive

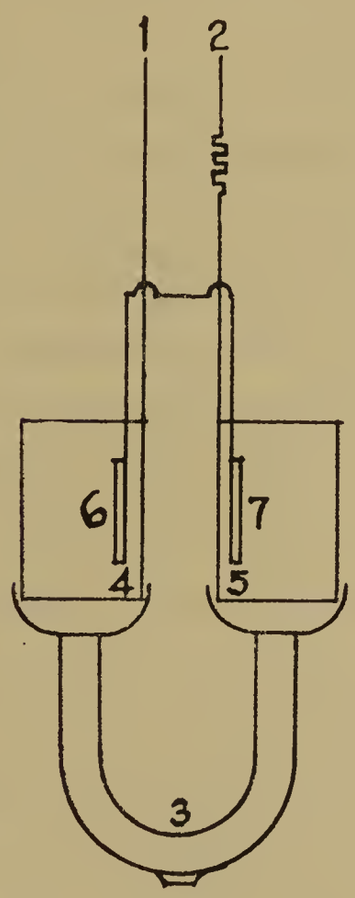

FIG. 2
Low voltage (220 v.) positive column lamp.

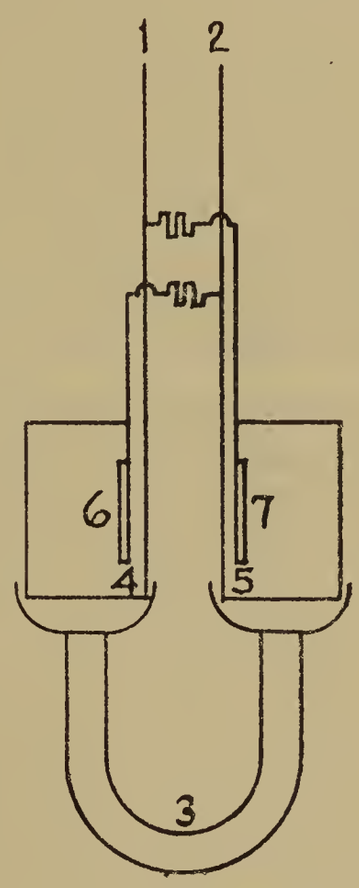

FIG. 4
Low voltage (110 v.) positive column lamp.

column lamps, that is immediately applicable to any 220 v. a. c. socket. Fig. 2 indicates its construction as well as one form of circuits that involve the fundamental principle of first generating in a short gap the electrons needed by the long positive column.

The line potential on 1 and 2, which are attached to the cylindrical electrodes 4 and 5, can not normally produce any current or any light through the long positive column 3; but there is provided the electrode 6, that is less than 1/64 in. from 4 and it is connected to a similar electrode 7, so that the 220 v.

immediately bridges the gaps 6-4 and 7-5, thereby generating electrons which then cause the 220 v. on 4 and 5 to produce a bright discharge through the positive column 3. One of the definitions of the word filament is "something continued in a long course" and since, when viewed from a short distance such a positive column discharge does not look unlike the carbon filament of a former type of series lamp, the term "gas filament lamp" has evolved in contra-distinction to a solid filament lamp. It will be noted that the gas filament is confined within a simple curved glass tube which has an opening or vent at its center. Since the bulb is supplied with neon gas at a pressure of about 20 mm., this vent not only tends to regulate automatically the gas pressure, within the filament tube, when it is warmed by the discharge, but also prevents electrode impurities, though small, from seriously affecting the gas filament conductivity. It might be called a self-healing or self-repairing conductor.

Fig. 3 is a photograph of such an experimental gas filament lamp suitable for 110 v., and Fig. 4 is a diagram of its construction and circuits. It will be noted that in the 220 v. lamp there are two ionizing gaps in series, and in the 110 v. lamp the gaps of each electrode are in multiple, which dispenses with all objectionable positive column resistance or its equivalent. A large number of modifications of both circuits and electrodes have been tried, with wattages varying from 1 to 100.

Life tests have proven that some of these lamps have, without appreciable change, run for over 500 hr. But it is not claimed in any sense that this new type of lamp has reached a commercial stage. This paper is written merely as a means of recording scientific advance in what has been claimed to be an important direction. Theory seems to indicate that to increase materially the luminous efficiency of light sources in general, resort should be made to radiation from gases electrically agitated.

Perhaps the exact and complete theoretical explanation of the action of these lamps is not now known, but it may suffice to say that at a definite line wattage consumption, a given lamp may satisfactorily operate without apparent change for several hundred hours, yet if operated at about 30 per cent lower watts its positive column will cease, due to lower gas pressure, and if

it is operated at about 30 per cent higher watts its positive column will also cease, but due to too high gas pressure. These actions suggest the query whether or not at the medium wattage there is going on a simple consumption of the electrode material, or is there a definite electrochemical cycle comparable to that of the Hg tube light.

Gas-filament light presents the possibility of higher efficiency than solid filament light, because (a) there is present no solid metal which requires energy to heat it, and (b) selective radiation can be employed far more easily. Not only theory but actual results conclusively show that inert gases are more efficient light producers than those that combine readily. This was indicated with nitrogen first, and later with neon, in which instance no energy is required to decompose molecules because it is monatomic. The problem of manufacturing short waves is simplified by utilizing a gas instead of a solid, because the electrons and ions are more free to vibrate. One can not discuss this problem of more efficient light production without touching upon the remarkable ability of a variety of fire-fly (*pyrophorous noctilicous*), which produces light at an efficiency of about 90 per cent.

It was about 1905 that I obtained from Cuba several dozen specimens to experiment upon. It is believed that the exact method is still unknown by which this animal accomplishes this remarkable result, but we do know that it is caused by the slow oxidation of fat, and that the essential elements are sodium or magnesia with formic acid and oxygen and water vapor, and that the light giving organs of the glow worm or fire-fly can be ground to an impalpable powder and then caused to reproduce a faint light by the addition of moisture. However, this subject has more to do with the production of light by purely chemical means, and it is believed that future generations may completely master this subject, but that at least our generation will be more familiar with the production of light by electrochemical means.

It is not generally recognized that a suitable gaseous positive column alone is a very efficient radiant, if the electrode losses are not taken into account, but with a gas filament lamp this electrode loss can easily amount to 30 per cent.

Our knowledge is not yet complete concerning the best scien-

tific manner of transferring the electric current from the solid leading-in wire to the gas-filament. Under some circumstances, this object is facilitated if the electrodes, or at least some portion of them, are maintained at high temperatures, but in the specific lamp under discussion it will be noted that the electrodes do not reach a temperature of red heat, in fact, they operate much below the melting point of the Mg, and are therefore sometimes spoken of as "cold."

The physical and chemical difficulties in connection with some of the other hopeful elements seem greater, and although most of the blank spaces of the table of the periodic law of the elements have now been filled in, still it is possible that some of the remaining elements to be discovered may be important in the solution of some of the problems of electrically agitated gas-lamps that have to do with both the electrodes and the conducting gas.

The fundamental data, that concerns each gas for this specific purpose, should be carefully tabulated, together with its action when coupled with various electrode materials and used at different pressures. I refer to conductivity, life, color, light-efficiency, etc. Many hundreds of experiments are involved in such a program.

CO_2 gas and aluminum do well, but nitrogen and aluminum result in a deposit of aluminum nitride throughout the entire length of a tube, one hundred feet long, for example, and Fe electrodes cause a deposit that cracks the glass tubing. The higher the frequency the more rapidly the gas disappears or is absorbed, and this is true even when vacuum tubes are investigated that are equipped only with exterior caps at their ends as electrodes.

After trying several hundreds of gas sources about two decades ago, the author stated that the theoretical results which were indicated as being obtainable from vacuum tube lighting would depend on the discovery of new elemental gases. Since then argon, neon, helium, xenon and krypton have been discovered.

All of these gases are interesting, but perhaps neon the most for gaseous conduction lighting, because of its low resistance and inertness. A two hundred foot Moore tube supplied with nitrogen will illuminate a large area efficiently, but if filled with neon the

necessary watts can be reduced about 75 per cent and the voltage 60 per cent, but the spectrum of neon, although it has few infra-red rays, has too much red and no blue. In speaking of this matter to the late Sir William Ramsay I thanked him for discovering such an important and interesting gas, but also asked him to "please find another gas, but get it white," in response to which he seriously replied, "It is not in the atmosphere, unless it is less than 1/25,000,000,000 of its volume."

The increasing attention that is being given to gaseous conduction throughout the world is clearly shown in the digests of the current technical journals, and in the large number of new mathematical papers dealing with various electronic theories. Many believe that electrical luminescence will be the next important stage in light development.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE PRODUCTION OF NITRIC OXIDES AND OZONE BY HIGH VOLTAGE ELECTRIC DISCHARGES.[1]

By Karl B. McEachron.[2]

Abstract.

The paper is a resume of a Bulletin of the Engineering Experiment Station of Purdue University, setting forth the results of a series of tests made on a number of different discharge tubes. The design of tubes was such that the action of glow, sparks and glow, and sparks alone could be studied separately. Tests were made with enclosed volumes of dry air and with moving air at different flow rates. The effect of pressure was also investigated. A new type of ozonizer was developed which produced high concentrations of ozone with only small yields of nitric oxides. The use of a mixed high voltage discharge produces, under favorable conditions, the higher oxides of nitrogen, which is desirable from the standpoint of absorption.

The material presented here is a review of the experimental work done by the Engineering Experiment Station of Purdue University up to the beginning of 1922.[3]

Very little commercial use has been made of the corona discharge which forms around a conductor when raised to a sufficiently high potential, although it has been known for many years that ozone and oxides of nitrogen were formed when the discharge took place in air. Some use has been made of ozone for bleaching, and for air and water purification. It has also had some use in medicine.

[1] Manuscript received June 14, 1923.

[2] Lightning Arrester Engineering Dept., General Electric Co., Pittsfield, Mass. Formerly Research Associate, Eng. Exp. Sta., Purdue University.

[3] See Bulletin No. 9 Engineering Experiment Station, Purdue University, for a detailed description of this work.

Attention at Purdue was first directed to the high-voltage corona discharge as a means of producing nitric oxides by an investigation by Spiel[4], who obtained a concentration, calculated as NO, of 5.6 per cent, when working with an enclosed volume of dry air in a Siemens ozonizer. Spiel found that when subjected to discharge, the pressure in the discharge tube first decreased to a certain minimum value, after which it increased. In many cases a pressure equal to or greater than the initial was reached. The greatest concentration of nitric oxides was

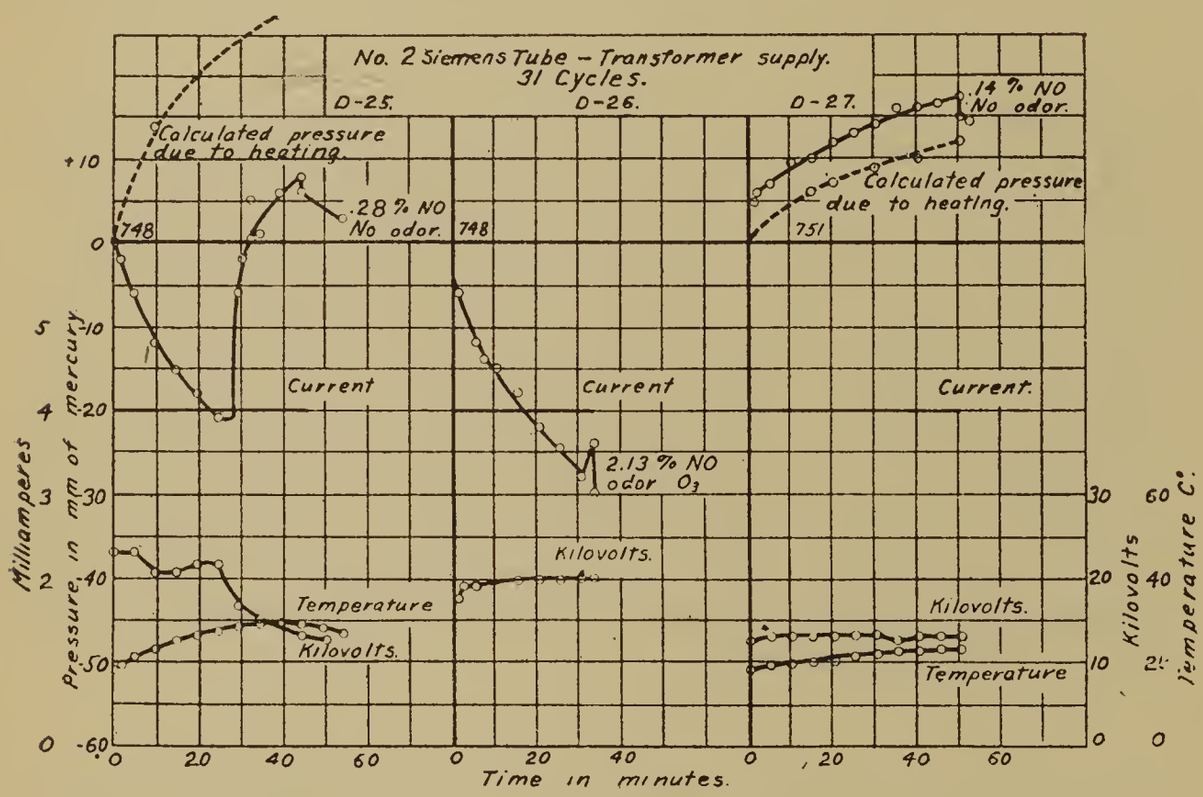

FIG. 1.
Runs D-25, D-26 and D-27.

found at the reversal point, while only very small concentrations could be found after the pressure had reached the initial. Spiel concluded that the product formed was N_2O_5.

The concentrations obtained by Spiel were high compared to those obtainable by the arc process of fixation, which made further investigation of the corona discharge desirable.

All of Spiel's work was done with an induction coil, making measurements of voltages and power rather doubtful. The natural starting point was to duplicate the Siemens tube used

[4] "The Formation on Nitric Oxides by the Silent Electric Discharge." Thesis submitted by Hugo Spiel at the Technical High School in Vienna, 1909.

by Spiel, and then extend the investigation to include other designs of tubes. Several of these tubes were constructed and a few of the results obtained for each tube are given in this paper.

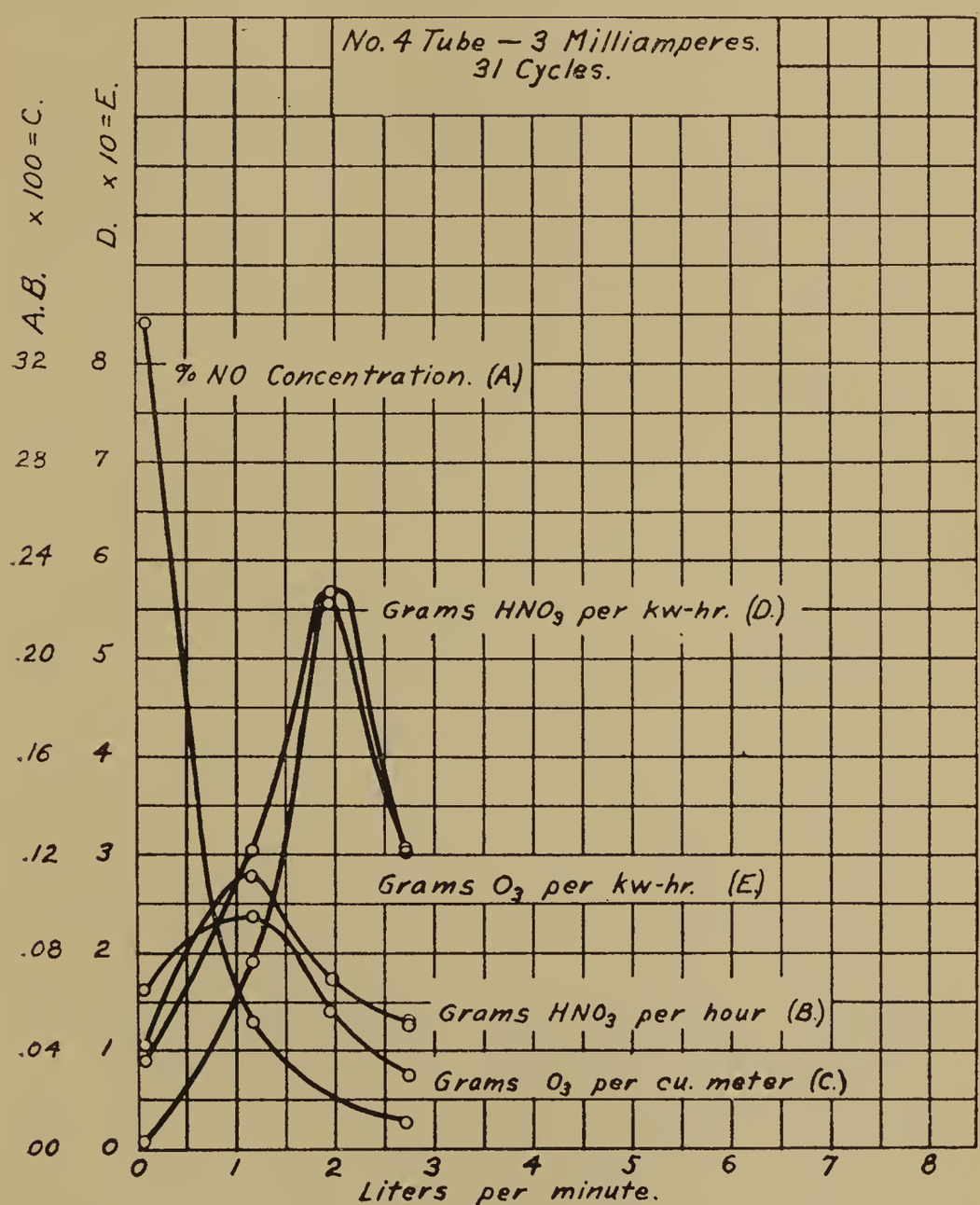

FIG. 2.
Yield Flow Curves.

I. RESULTS OF TESTS ON A SIEMENS TYPE TUBE[5].

This tube was made primarily to check Spiel's results and at the same time to try the effect of using alternating current, in which case measurements of potential and the energy used could be made.

[5] The nitric oxides were absorbed in NaOH. All concentrations of nitric oxides are based on the amount of HNO_3 observed, but expressed as NO.

In Fig. 1 may be seen curves which are more or less typical of all the tests made. Run D-25 on the left of the figure shows the pressure reversal, which was found in all cases where the pressure decreased. The temperature shown is that of the inner

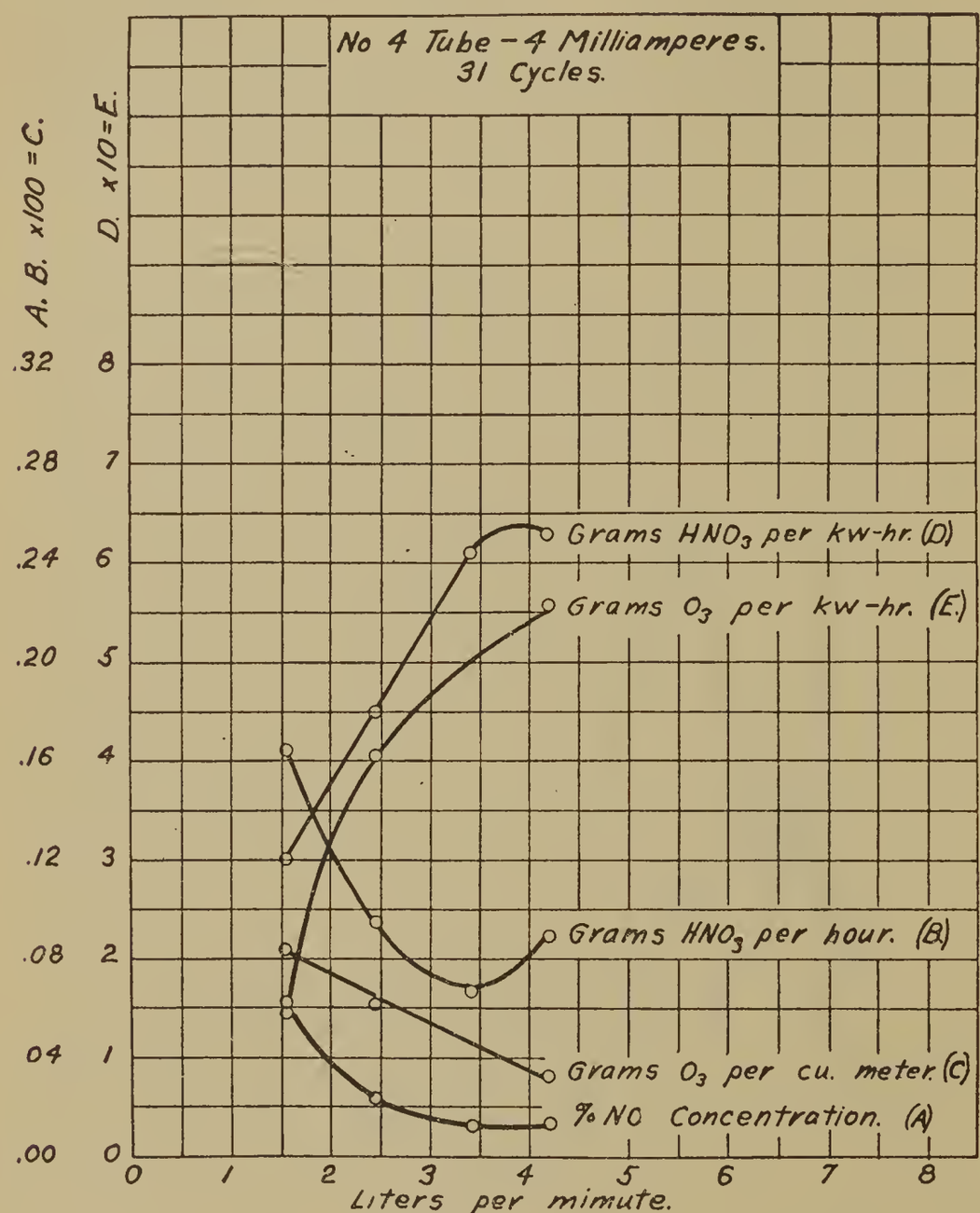

FIG. 3.
Yield Flow Curves

electrode, which was not water-cooled. Only a small concentration of NO was obtained at the end of the run, while in the check run D-26 a concentration of 2.13 per cent NO was obtained at the reversal point.

If, instead of applying voltage to the tube immediately after sweeping out with fresh dry air, the tube was allowed to stand several hours, the pressure characteristic was changed altogether. This condition is shown in run D-27 on the right of Fig. 1.

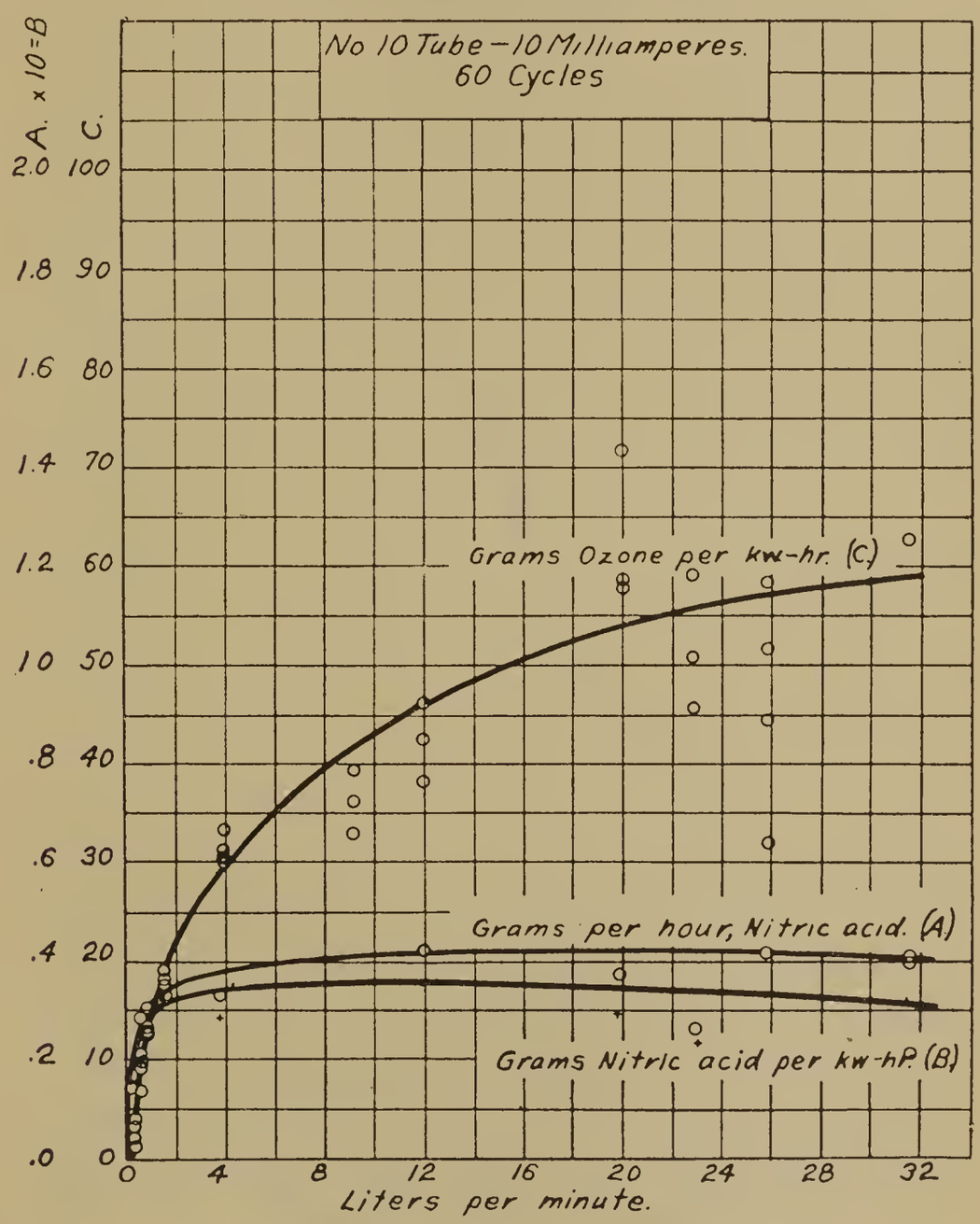

Fig. 4.

Yield Flow Curves—Ozone and Nitric Acid.

The pressure decrease in some cases was considerable. In one run, which has not been duplicated, the pressure decreased from 750 to 636 mm. with an NO concentration of only 1.42 per cent. These figures are not corrected for temperature change.

Conclusions from Tests on Siemens Type Tubes.

1. To determine the concentration at the reversal point in a run in which the pressure is allowed to reverse and rise to the

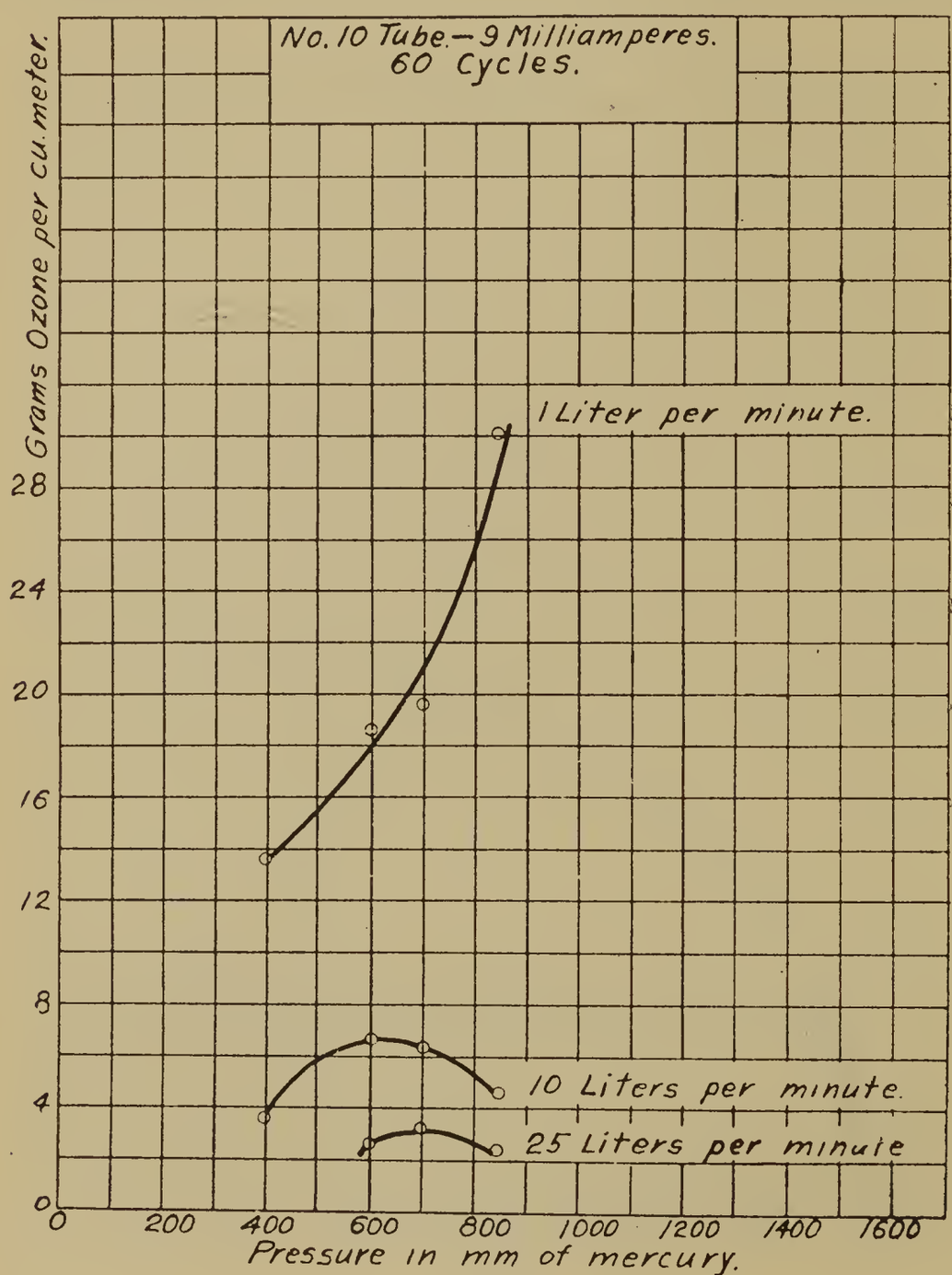

FIG. 5.
Yield Pressure Curves—Ozone

initial or higher pressure, it is necessary to stop a check run at the reversal point and absorb the products formed. As a result of the tests made, it is concluded that such a procedure will give only approximate results for the reversal point. It was found

that two runs made under as near the same condition as possible show considerable variation as to time of reversal and the amount of pressure decrease at which it took place. If both runs are

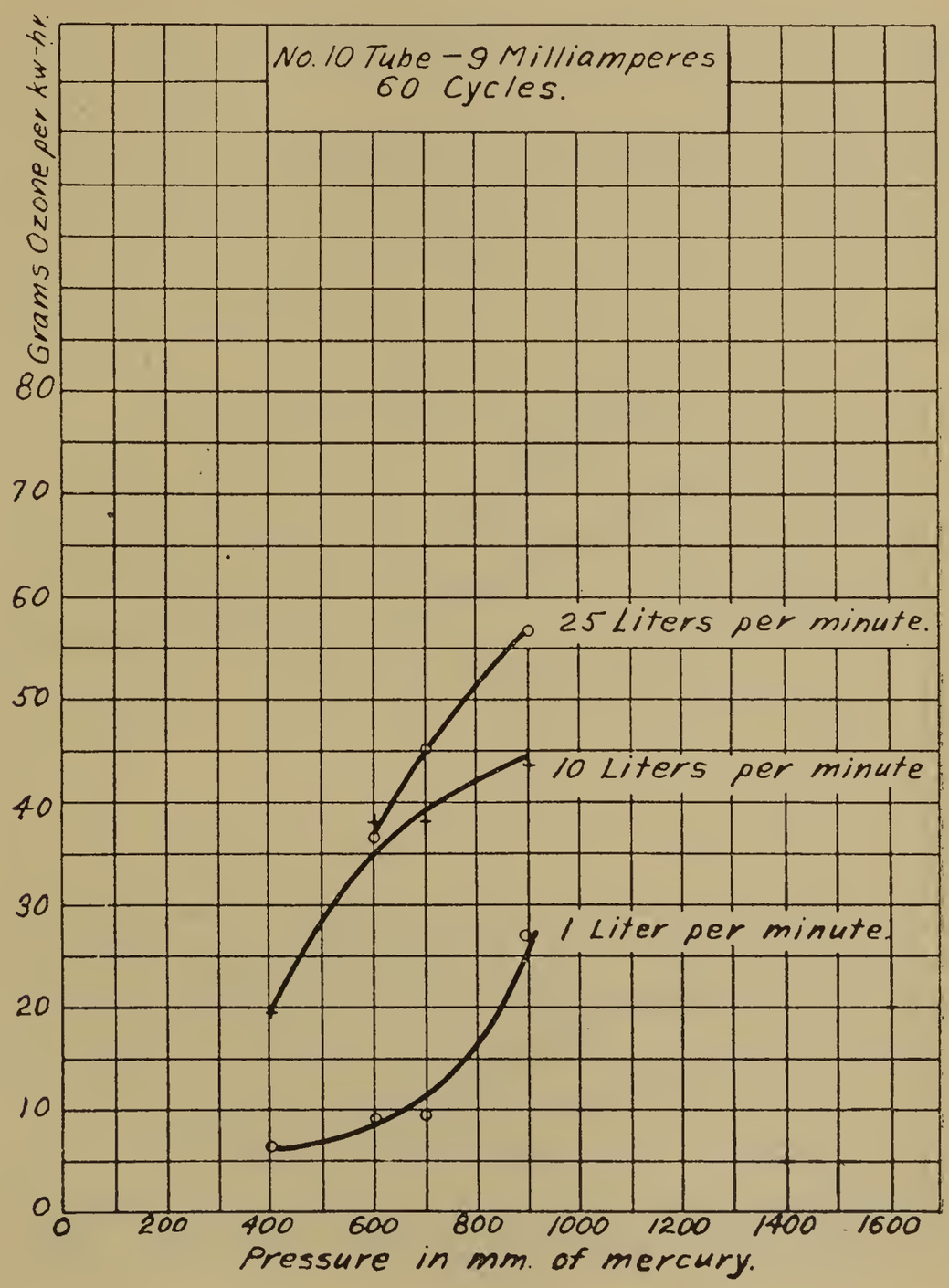

FIG. 6.
Yield Pressure Curves—Ozone

stopped at the reversal point, the concentrations are usually quite different.

2. When air in the tube has been in contact for a considerable period with other air which has been previously subjected to an

electrical discharge, the usual pressure decrease is modified, the yields diminish, and in case sufficient contamination has taken place, the characteristics of the tube will change altogether, the

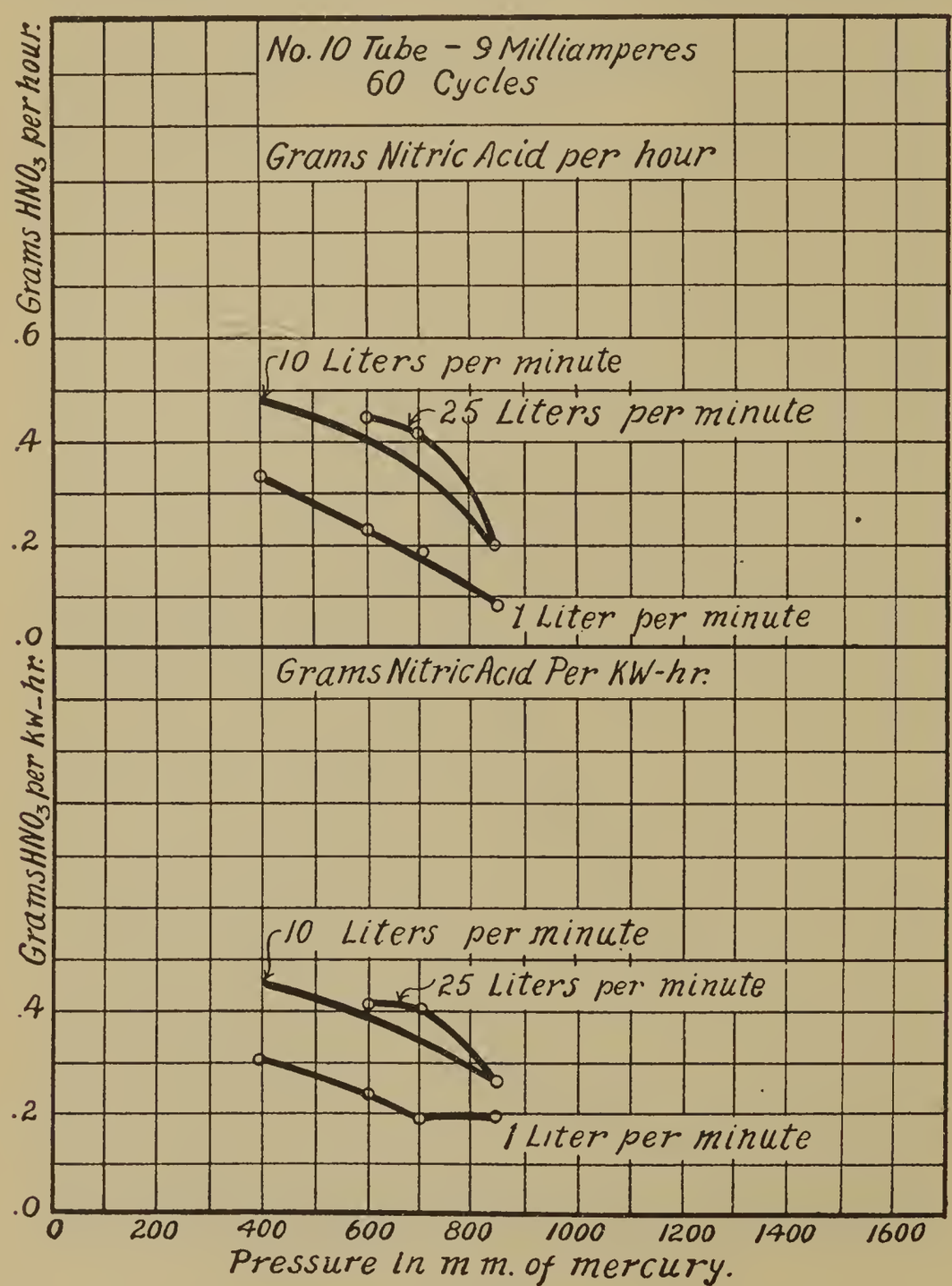

FIG. 7.
Yield Pressure Curves—Nitric Acid.

pressure increasing instead of decreasing and the yield being greatly diminished or eliminated altogether.

3. The pressure decrease is not proportional to the nitric oxides and ozone absorbed. The pressure decrease is always

greater than can be acounted for by the products obtained, showing a decrease in the number of molecules in excess of the calculated value.

II. DISCHARGE TUBES OF THE ROD TYPE: SMALL GLASS TUBE.

This tube differs from the Siemens tube in that the annular space between the two glass tubes is much greater and is filled with a discontinuous dielectric material, which, in this case, consists of a large number of glass rods extending throughout the length of the discharge tube. The tube had a measured volume of 259 cc.

Results of Tests[6].

The curves in Fig. 4 and 5 show some of the results of tests made on the tube when dry air was circulated at varying rates. The best yield of nitric acid was 6.4 g. per kw-hr. The best ozone yield was 56.7 g. per kw-hr., with a concentration of 5.6 g. per cu. m.

The study of a small tube of this type leads to the following conclusions:

1. That such a tube will give uniform discharge, without the formation of sparks.

2. Increasing velocity will reduce the concentration of both ozone and nitric oxides, and will increase, up to a certain limit, the yield in grams per kw-hr. This means that this type of tube follows the same general characteristics as other tubes made for the utilization of the corona discharge.

3. The ozone yield is high enough at 31 cycles to warrant further investigation of this type of tube as an ozonizer, some of the yields comparing favorably with the published results of other tubes.

Large Rod Type Tube[7].

This tube consisted of a porcelain tube 1.5 m. in length. The electrodes consisted of two aluminum tubes, one inside and one

[6] The ozone yields were obtained by absorption in KI and titrated with $Na_2S_2O_3$.

[7] For details of construction of this tube and the absorption apparatus see pages 72 and 165, Bulletin No. 9, Eng. Exp. Sta., Purdue University.

outside the porcelain tube. The space between the porcelain and aluminum tubes was filled with long glass rods. The absorption apparatus was improved considerably for use with this tube. Briefly, water and the gas to be absorbed are forced through a nozzle into an inverted carboy, producing a very fine spray, which gave excellent absorption.

Considerable fog was produced in the absorption apparatus under certain conditions. This was condensed and collected by passing the gas, leaving the carboy, into a small chamber where its direction of flow was abruptly changed. In some cases the titration of this condensed fog showed it to be stronger than normal acid.

Results of Tests.

Runs were made at 8, 9, 10 and 11 mili. amp., and at pressures ranging from 400 to 845 mm., the rate of air flow being varied in each case. The yield of ozone and nitric acid for a pressure of 845 mm. and a current flow of 10 mili. amp. is shown in Fig. 4. The effect of change of pressure for ozone is shown in Fig. 5 and 6, and for nitric acid in Fig. 7.

The following is a partial summary of the results of the tests.

1. Increase in current from 8 to 9 mili. amp., increased the ozone concentration and yield per kw-hr. considerably. Further increase in current resulted in increased concentration up to the 11 milliampere point where the concentration at low velocities fell off, while that at the high velocities remained practically constant. The yield per kw-hr. of ozone reached a maximum between 9 and 10 mili. amp.

2. The yield of ozone decreases with decrease in pressure.

3. With decreasing pressures (from 845 mm. to 400 mm.) the yield per kw-hr. of nitric acid shows considerable increase.

4. One of the best average yields of ozone, taking both concentration and efficiency into account, was made with an air flow rate of 90.9 L. per min., the pressure and current being 845 mm. and 10 mili. amp., respectively. The yield from this run was 66 g. per kw-hr., with a concentration of 6.5 g. per cu. m.

In the same run the NO concentration was 0.0139 per cent, with a yield of nitric acid per kw-hr. of 2.9 g.

5. The only long run made, something over five hours in duration, showed that some form of cooling is probably needed to prevent a decrease in yield due to the increased temperature of the tube.

III. TESTS ON A LARGE SINGLE DIELECTRIC TUBE.

The tube consists of an aluminum rod, 1.59 cm. in diameter, surrounded by a porcelain tube, 7.6 cm. inside diameter and 10.1 cm. outside diameter, which in turn is arranged inside an aluminum tube 14.4 cm. in diameter, all parts being positioned concentrically. The active length of the tube is 152 cm. The voltage used varied from 47 to 60 Kv., depending on the pressure. The energy taken by the tube was kept constant throughout the test.

Since much of the work with this tube has already been published in a paper before the A. I. E. E. in 1920, as well as in Bulletin 9, only a brief summary of the results will be included.

Results of Tests.

1. This tube gives a mixed discharge consisting of corona with quite a large number of static sparks, which decrease in number and length with decreasing pressure.

2. With an increase in air velocity at pressures slightly above the atmosphere, the nitric acid yield increases rapidly, a peak being formed at an air flow rate of about 6 L. per min.

3. In general, the ozone yield increased with increasing air velocities, but suffers a decrease at about the same air flow rate at which the nitric acid curve shows a maximum.

4. The yield of nitric acid decreases with diminishing pressure.

5. In general, the yield of ozone increases with a decrease in pressure.

6. A white fog containing nitric acid appears over the absorption liquid in varying densities and remains for varying lengths of time, depending upon the pressure and the air rate.

The fog was first collected while working with this tube, and Fig. 8 shows the amount of increase in yield due to the collection of this fog.

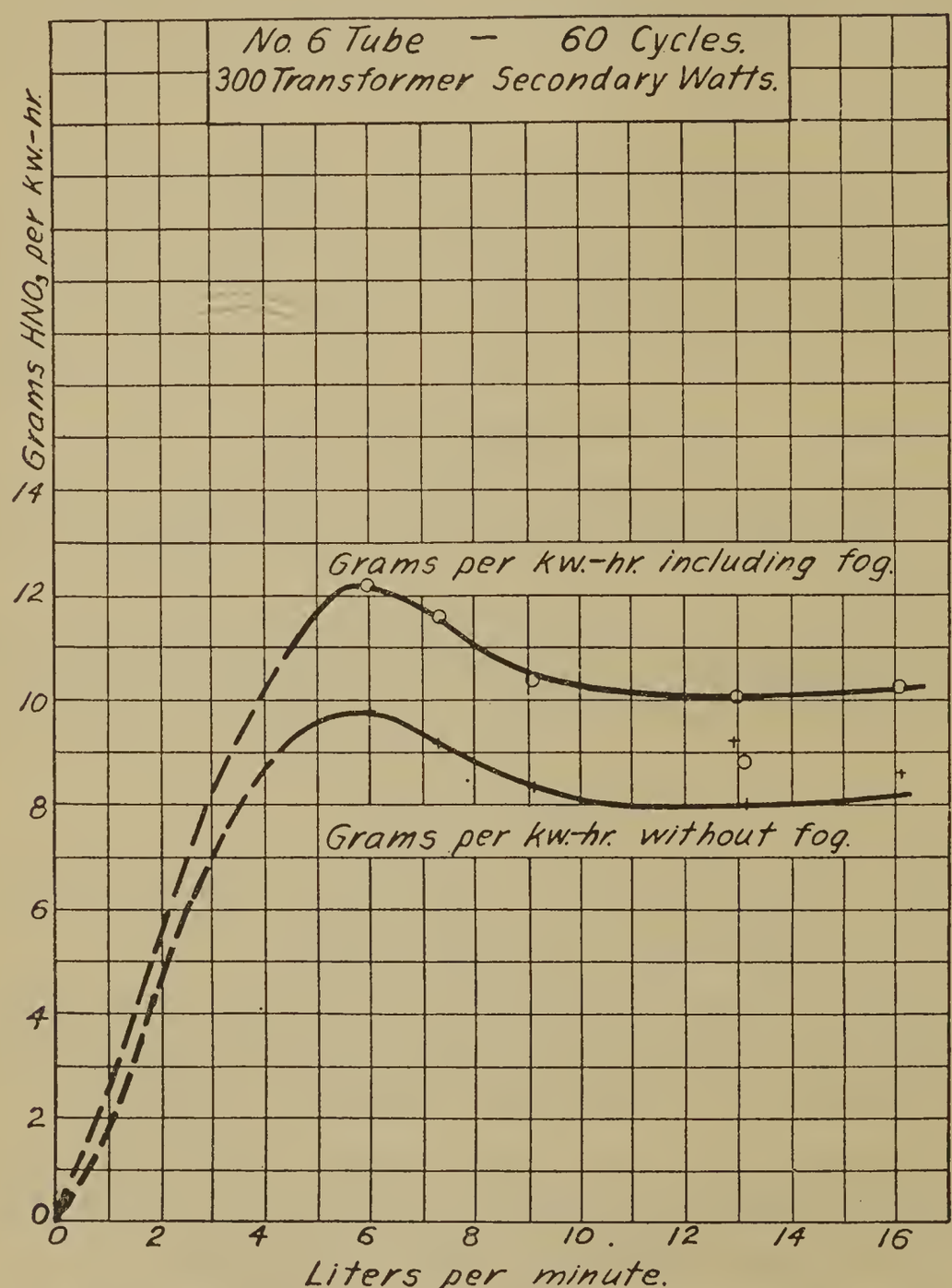

FIG. 8.
Increase in Yield Due to Collection of Fog.

IV. TESTS ON A TUBE USING SPARK DISCHARGES.

One of the results of the design of the rod type tube was to suppress the formation of static sparks, and from the large tube of this type considerable yields of ozone were obtained with

very small yields of nitric oxides. With a tube in which sparks occur frequently, as in the large single dielectric tube, a much higher concentration of NO was obtained, ranging from about

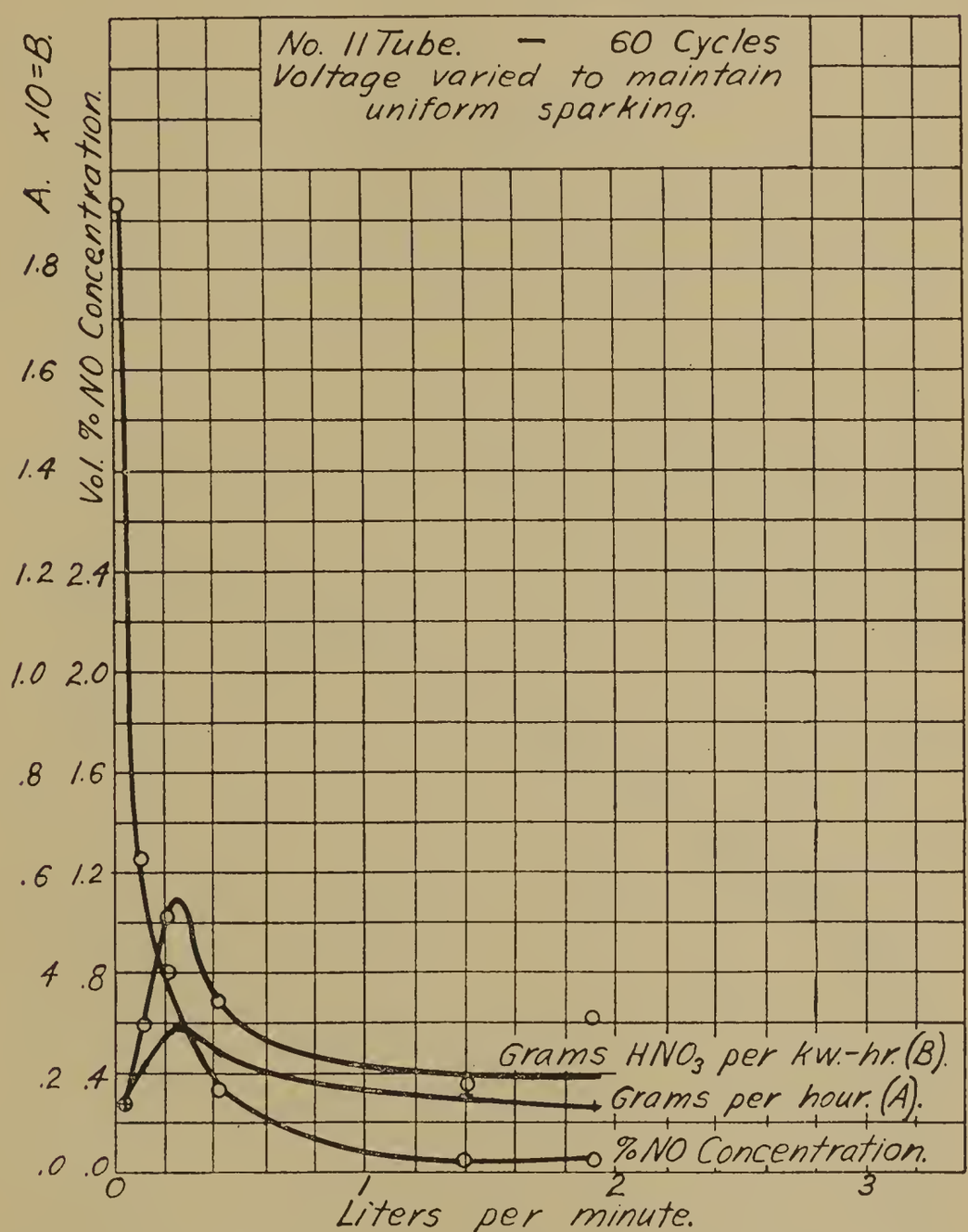

FIG. 9.
Yield Flow Curves at 895 mm.—Nitric Acid.

twice, at low velocities, to about three times as great at higher velocities.

A small discharge tube was constructed of glass tubing approximately 5 cm. in diameter and 35 cm. long. The discharge took place between the ends of No. 14 aluminum wires, care-

fully pointed and spaced 10 cm. apart. Measured dried air was passed through the space between the rubber stoppers, placed in the ends of the tube, and then conveyed to the absorption chamber containing NaOH.

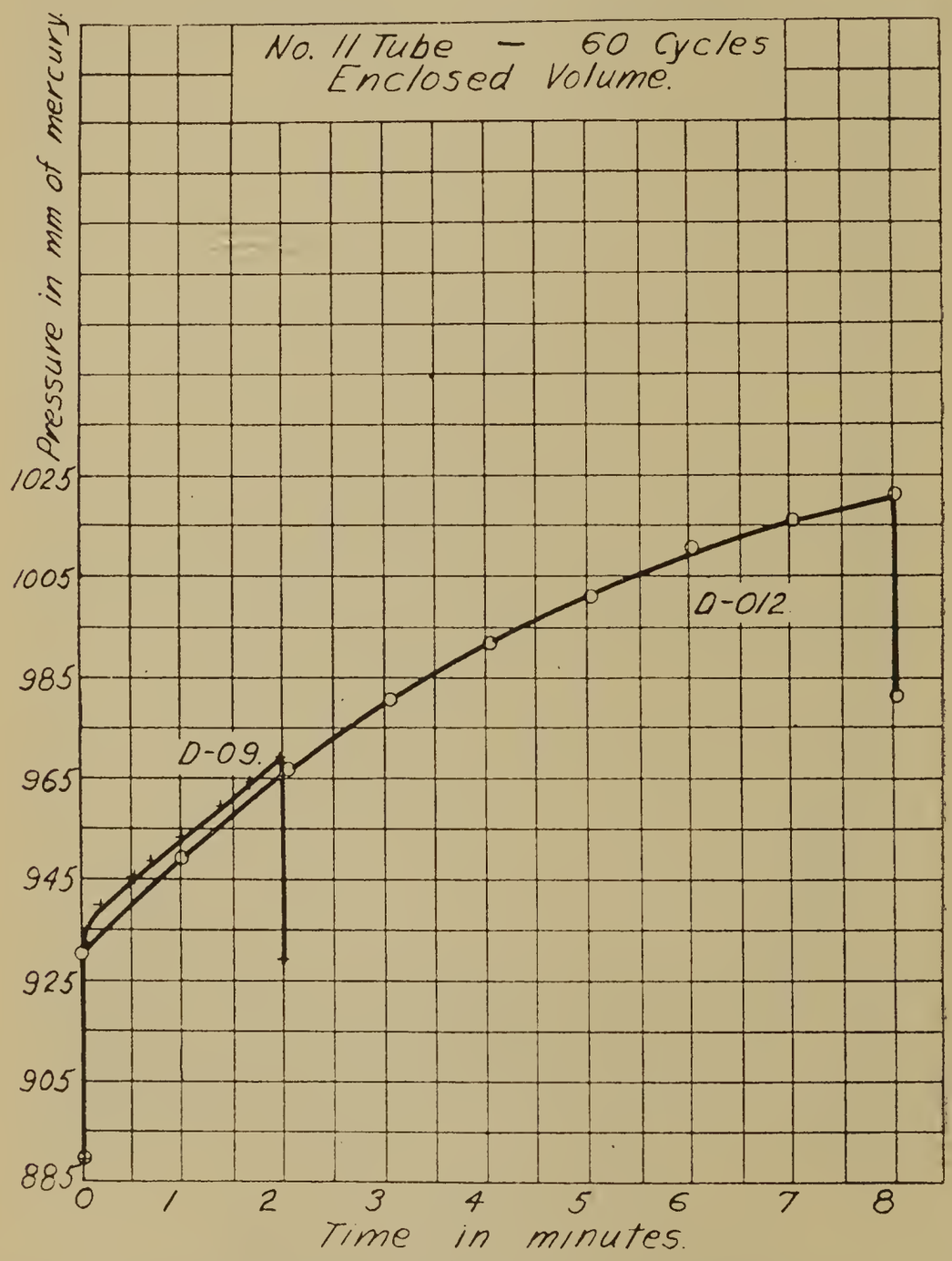

Fig. 10.

Pressure Time Characteristic—Runs D-09 and D-012.

Results of Tests.

The results of the tests with moving air are shown in Fig. 9. The highest concentration obtained (3.87 per cent NO) from

any type of tube using moving air was obtained with an air flow rate of 0.0187 L. per min.

With all of the runs having a concentration of NO above one per cent, a yellowish-brown coloration was perceptible in the tube, indicating the presence of NO_2. With the run mentioned above, in which a concentration of 3.87 per cent was observed, the brown color was very pronounced.

The pressure characteristic with an enclosed volume of air is interesting and is shown in Fig. 10. There is a pressure due to the spark of nearly 40 mm. of mercury. This type of tube produced only very small yields of ozone.

V. GENERAL CONCLUSIONS.

1. The previous electrical history of the gas has a marked effect on the character of the discharge and the products formed.

2. Traces of the products of previous runs, made in small tubes of the Siemens type, modify the character of the discharge and decrease the absorbable products.

3. Increase of current flowing in the discharge increases the yields of both ozone and nitric acid up to a certain maximum, beyond which further increase in current decreases the yields.

4. With increase of pressure the yields of ozone increase until a pressure near the atmosphere is reached. At higher pressures the yields in general decrease.

With increasing pressures, within the limits investigated, the yield of nitric acid increases with tubes, in which sparking occurs, and decreases in tubes, like the rod tubes, in which sparking does not occur.

5. Increase in rate of air flow will in general increase the yields of nitric acid up to a certain maximum, the critical air flow rate being dependent upon the tube used. Increased air rates give increased yields of ozone which tend to become constant at higher rates.

6. Sparks passing through air cause a pressure increase much too rapid to be a heat effect. This effect has been mentioned by J. J. Thompson and others.

7. With an enclosed volume of air a pressure decrease occurs at the instant the power is disconnected, which is the pressure change due to ionization noted by Farwell and others.

8. A tube of the rod type, if properly cooled, gives yields of ozone of sufficient magnitude, so that the tube becomes of importance as a commercial ozonizer.

9. In air, the corona discharge favors the production of ozone, while sparks tend to produce oxides of nitrogen. Some exceptions may be found to this, as in the Siemens tubes where the yield of N_2O_5 was at times quite large, and yet the discharge consisted of only a fine glow.

It might also be pointed out that a combination of sparks and corona produces the higher oxides of nitrogen, which are desirable from the absorption standpoint.

DISCUSSION.

R. H. George[1]: In Mr. McEachron's conclusions concerning the work on the Siemens tube, the statement is made that the pressure decrease is always greater than can be accounted for by the nitric acid and ozone obtained. This conclusion, as I recall, is based on the assumption that the products remain in the gaseous state. The discrepancy between pressure decrease and yield was thought to be due to the formation of a heavy molecule.

In some recent experiments conducted at Purdue University, in which enclosed volumes of air enriched with oxygen were circulated in a closed system consisting of a discharge tube and cooling chamber, some of the products were condensed out at temperatures as high as 20°C. From these results it appears that some of the products of the discharge in the Siemens tube might have condensed and given abnormal decreases.

In the case of the tests in which the gas was cooled, a clear oily liquid condensed out first which was converted to acid-forming oxides as the run progressed. When the tests were of sufficient length the pressure decrease was accounted for by the acid and ozone obtained. If any of the liquid remained on the surface of

[1] Research Asst., Engineering Experiment Station, Purdue Univ., Lafayette, Ind.

the glass after the apparatus had been swept out following a run, it slowly decomposed into lower oxides of nitrogen. When voltage was applied to the gas in this condition no excess of ozone was formed and the pressure increased. Therefore, it is now thought that this liquid product is largely responsible for the erratic results obtained in the earlier investigation.

F. A. LIDBURY[2]: Were dry gases used in these experiments?

K. B. MCEACHRON: Yes.

R. H. GEORGE: In our recent experiments the gas was passed through concentrated H_2SO_4, soda lime, and a long U-tube filled with P_2O_5, before entering the discharge apparatus. The apparatus was dried by passing dried gas through it for 2 or 3 hr. No heat was applied.

FRANK E. HARTMAN[3]: At one time we used bakelite dielectrics and made no attempt to dry the air. We were compelled to discontinue this practice, however, due to the precipitation of moisture on the dielectrics and the absorption, by the precipitated moisture, of the oxide of nitrogen produced in the generator. The net result was the production of nitric acid on the dielectric material, which rapidly brought about its deterioration. In fact we have observed small beads of moisture on a dielectric that had been used but a short time when no precautions were taken to dry the air. We came to the conclusion that it was necessary to dry the air, as much as possible, and always consider that any liquid present in the generator was due to the precipitation of moisture from the air. At present we use calcium chloride dryers. The air produced by them has a relative humidity of 5 or 6 per cent at 21°C., and the use of this air had been very satisfactory, largely eliminating dielectric rupture. When using air, however, of a relative humidity from 45 to 60 per cent at 21° C. the formation of nitric acid on the dielectric proceeds so rapidly that the operation can be continued only a short while before rupture occurs.

F. A. LIDBURY: Possibly the moisture comes from the glass.

R. H. GEORGE: There is a possibility of traces of moisture coming from the glass itself, and also a possibility of the grease

[2] Works Manager, Oldbury Electrochemical Co., Niagara Falls, N. Y.
[3] United States Ozone Co., Scottdale, Pa.

used on the stopcocks being decomposed and uniting with the products of the discharge. The moisture content of the gas should be very small after passing through the P_2O_5.

COLIN G. FINK[4]: As to getting moisture from the grease of a stop-cock, we were working with SO_3, and we first attributed the source of the moisture to our oxygen, but we eliminated it from the oxygen by bubbling through liquid sodium, which is even a little more efficient than P_2O_5. Then we used a special, so-called gas-free, glass and finally we traced the moisture right back to the stop-cock grease. We eliminated the grease and used P_2O_5 as "grease" and then obtained very good results[5].

R. H. GEORGE: We have been recently considering the use of H_3PO_4 and P_2O_5 as a stop-cock lubricant. Up to the present we have used white vaseline. However, the volume of stop-cock grease in contact with the gas would not amount to more than 1/10 or 1/15 the volume of liquid obtained from the long runs.

[4] Head, Div. of Electrochemistry, Columbia Univ., New York City.
[5] Z. physikal Chem. 60, 1 (1907).

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

SURFACE COMPLICATIONS IN THE CORONA DISCHARGE.[1]

By F. O. Anderegg.[2]

Abstract.

Quantitative knowledge of chemical reactions in the corona discharge is meager because, for one important reason, of complications at the surfaces. serious enough in certain cases to alter completely the nature and products of the discharge. A variety of metallic and dielectric surfaces has been studied, and the conclusion is reached that all materials should be carefully tested for reliability before use. An explanation of the pressure reversal produced by a discharge through enclosed air is given in the light of the experiments described.

A careful study of the literature covering ozone formation and other chemical reactions in the corona discharge brings to light certain unexplained deviations in the results, which are much greater than the variations in the supply of electrical energy or in the other conditions would lead one to expect. It is the purpose of this article to present evidence, obtained in working with different types of discharge, that the variations noted are due, to a greater or less extent, to disturbing effects at the walls of the apparatus.

In order to secure effective chemical action in a corona discharge, especially at atmospheric pressure, the discharge density must be large; therefore a narrow space is used. This results in a rather large ratio of surface to volume, (specific surface), so that such phenomena as adsorption of gases on solid surfaces may introduce complications which are more or less serious. Photo-

[1] Manuscript received June 13, 1923.

[2] Dept. of Chemistry, Purdue University, Lafayette, Ind.

electric fatigue,[3] the overvoltage in electrolysis,[4] the polarization of x-ray bulbs,[5] the importance of removing the adsorbed gas film in vacuum discharge technique and the clean up of gases at solid surfaces,[6] are all examples of similar effects.

DIRECT CURRENT CORONA.

While studying the formation of ozone in pure oxygen by a direct current discharge in 1917,[7] the first example of surface complication was met by the writer. A platinum wire was placed

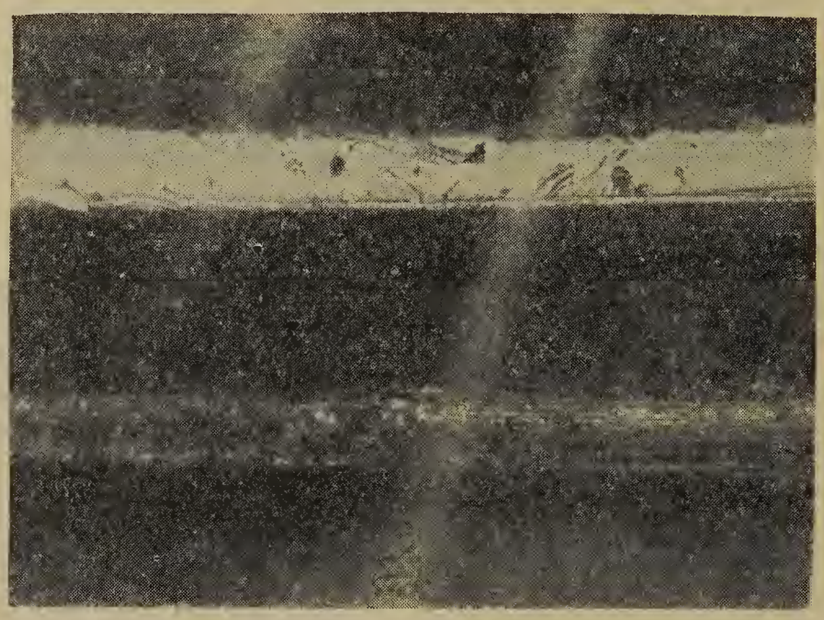

FIG. 1.—A No. 29 platinum wire (× 50). The lighter wire is the end of the wire which had not been in discharge. The darker wire had been used as electrode in direct current discharge. Note the finely divided material on the dark wire.

concentrically within a cylindrical gold foil of 1.8 cm. diameter. After the apparatus had been in use for some weeks it was noted that during discharge through oxygen enclosed within the tube

[3] W. Hallwache, Physik. Z. **21**, 561 (1920); L. A. Welo, Phil. Mag. **45**, 593 (1922).

[4] Bancroft, Applied Colloid Chemistry. p. 23 (1921). Marsh and Evans, Proc. Roy. Soc. **102**, 328 (1922).

[5] S. Ratner, Phil. Mag. **43**, 193 (1922); R. Whiddington, *ibid.*, **43**, 720 (1922). A. Janitzky, Z. Physik. **1**, 22-30 (1922). Relation between adsorbed films and electric discharge.

[6] Research Staff of the General Electric Co. Ltd., Phil. Mag. **40**, 585 (1920); **41**, 685 (1921); **42**; 227 (1921); **43**, 914 (1922). F. H. Newman, Proc. Phys. Soc., **32**, 190 (1920); **33**, 73 (1921); Phil. Mag., **44**, 215 (1922). H. E. Farnsworth, Phys. Rev., **20**, 358 (1922). Other references of the same general nature; W. Schottky, Z. Physik, **14**, 63-106 (1923), Cold and Hot Electron Discharges. J. Zeleny, Phys. Rev., **19**, 566 (1922), Point Discharge and Adsorbed Films. I. E. Goldstein. Ber. physik. Ges., **20**, 123 (1918). The Appearance of the Discharge Varies with the Arrangement of Surface. Millikan et al. Phys. Rev., **18**, 236 (1921), Contact Potentials. A. Bailey, *ibid.*, **20**, 154 (1922), Resistance of Adsorbed Films to High Frequency Current. Two pertinent references; R. W. Wood, Phil. Mag., **44**, 538 (1922) and R. Seeliger, Z. Physik., **15**, 27 (1923) on the catalytic recombination of hydrogen atoms.

[7] J. Am. Chem. Soc., **39**, 2851 (1917).

an ever increasing voltage was required to maintain a constant current strength.[8] The first run each day gave also a low yield of ozone. On repeating, increasing values were obtained from run to run until the yield was normal. To overcome this "lag" effect it was customary to make a preliminary run of 20 min.

This work was repeated by A. C. Grubb[9] and J. K. Stewart[10] who both used the same kind of apparatus, but the current was

Fig. 2.

Fig. 3.

Fig. 2—A gold foil (× 50) that has not been subjected to the discharge.

Fig. 3.—Some of the same foil after serving as electrode in the discharge with the platinum wire of Fig. 1.

rectified by a kenotron instead of coming from direct current generators. Both observed that new electrodes without previous use as electrodes gave neither of these effects until after 10-20 hr. of use. The electrodes that were used longest have been microphotographed by Dr. E. G. Mahin, and are reproduced in Fig. 1, 2 and 3. A marked change in the physical condition of the electrodes is observed, somewhat similar to the surface changes which

[8] Cit. 7, Fig. 2.

[9] A. C. Grubb, Thesis, Purdue University, 1919.

[10] J. K. Stewart, Thesis, Purdue University, 1920.

are produced during the activation of a platinum catalyst used in ammonia oxidation.[11]

HIGH FREQUENCY CORONA.

Similar effects have been noted when a high frequency discharge was passed between an aluminum tube 4.65 cm. in diameter and a concentric platinum wire.[12] Copper gave less trouble than platinum, while with an aluminum wire no lag effect was observed. This indicates a specific adsorptive effect, depending upon the nature of the material.

SIEMENS TUBE EXPERIMENTS.

Hugo Spiel has studied pressure changes produced on passing a silent discharge through air enclosed within a Siemens' ozonizer.[13] After a period of decreasing pressure a sudden reversal was noted. Part of this work was repeated by the writer in 1918, and the actual existence of such a reversal was confirmed. This remarkable phenomenon has since been studied at this University more fully by McEachron and George.[14] An attempt is made in this paper to offer an explanation based on additional experimental evidence.

THE CREEPAGE CORONA.

When a dielectric material is placed in a field of force the field is distorted, according to the well known laws of electrostatics.[15] When tested out experimentally with spark or corona discharge, surface effects are superimposed,[16] however, which may be of greater magnitude than the pure electrostatic effects. The marked differences in results between glass fragments and glass wool tubes, given below, will emphasize this point. A study of some of these surface effects has been made with air flowing through the discharge tube, and also with air enclosed within the tube. To complete the study, results obtained without any dielectric fragments are included.

[11] Rideal and Taylor, Catalysis in Theory and Practice, p. 97, 1919.

[12] F. O. Anderegg, Proc. Indiana Acad. Sci., 157 (1921).

[13] Hugo Spiel, Thesis, Vienna, 1909.

[14] K. B. McEachron and R. H. George, Purdue University Expt. Sta. Bull. No. 9, 22-56 (1922).

[15] Jeans, Electricity and Magnetism; and other texts.

[16] C. W. Rice, Trans. Am. Inst. Elec. Eng. 36, 1947-50 (1917). McEachron and George, cit. 14, pp. 58-108.

In these experiments new Liebig condensers were used, except for one pyrex glass tube. These were made of ordinary soda-lime glass, with an inside diameter of 1.0-1.1 cm., a wall thickness close to 1 mm. and a water jacket of 50 ± 1 cm. long, which served as outer electrode and temperature regulator. An aluminum wire was placed at the axes of each tube as inner electrode. The

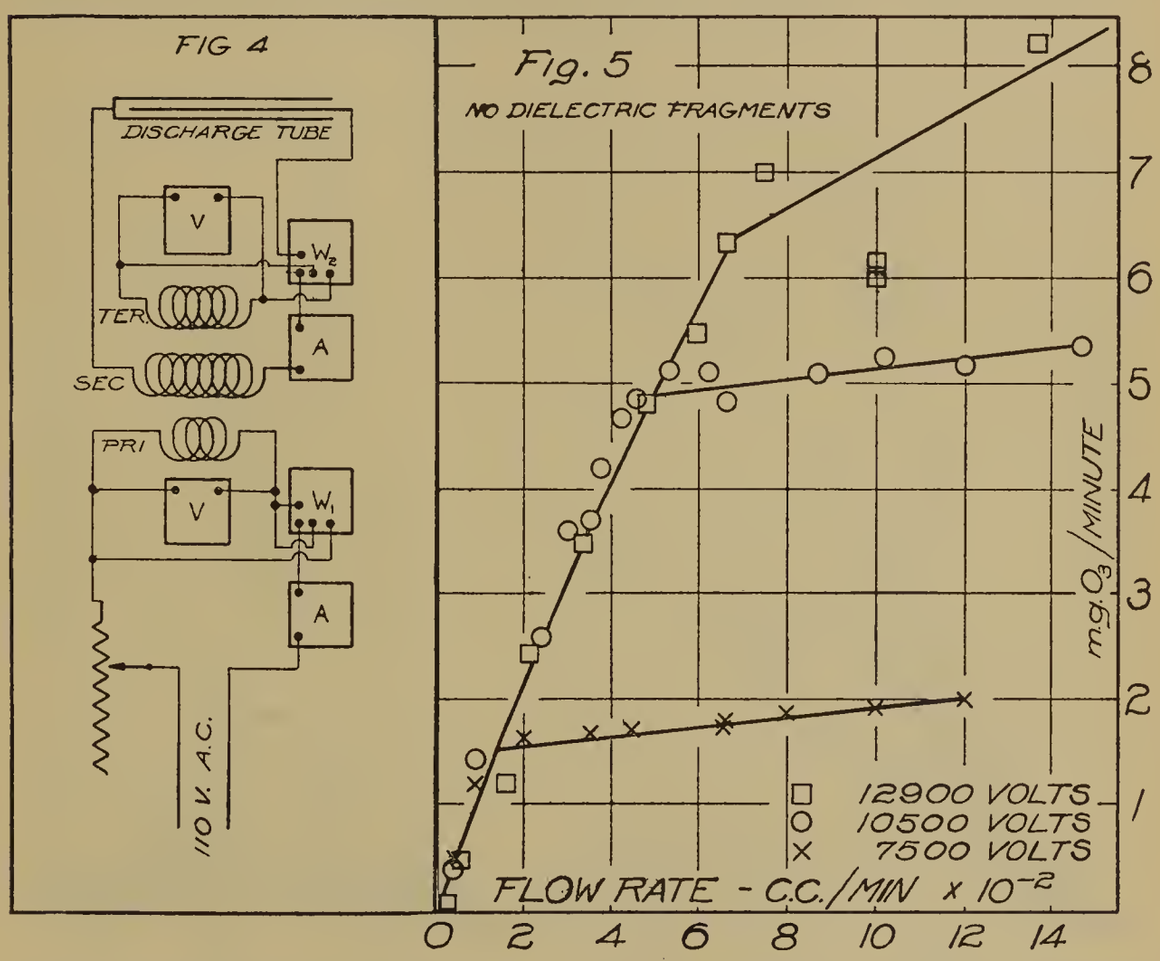

FIG. 4.—Electrical connections. A Thordarson transformer without any tertiary coil was also used for part of the work.

FIG. 5.—In a Liebig condenser a No. 24 aluminum wire serves as an inner electrode, the water in the jacket acting as the other electrode. The yield of ozone in mg. per min. was determined for varying flow rates at three voltages. At low flow rates the ozone is decomposed by the accumulation of nitrogen compounds.

apparatus was all of glass except at the points where the aluminum wires came through, where a little special resistant wax was used.[17] The liquid in the manometers was a high grade saturated paraffin oil. The pressure at the start of all runs was 750 mm. Dry air, free from carbon dioxide, was used. Nitrogen pentoxide was absorbed in 0.01 *N* alkali and the ozone in aqueous solution of potassium iodide.

[17] The wax contains rosin, sealing wax and beeswax.

Runs with flowing air included three tubes with B. & S. No. 6, 24 and 36 wires and no dielectric fragments.[18] The results are recorded in Fig. 5, 6 and 7. The sharp breaks in the curves in Fig. 5 are explained by the accumulation of substances at the lower flow rates, which cause decomposition of ozone. The results described below make it seem likely that lower oxides of nitrogen are the negative catalysts. The yields of ozone for low flow rates are the same for different voltages. With increase in size of wire

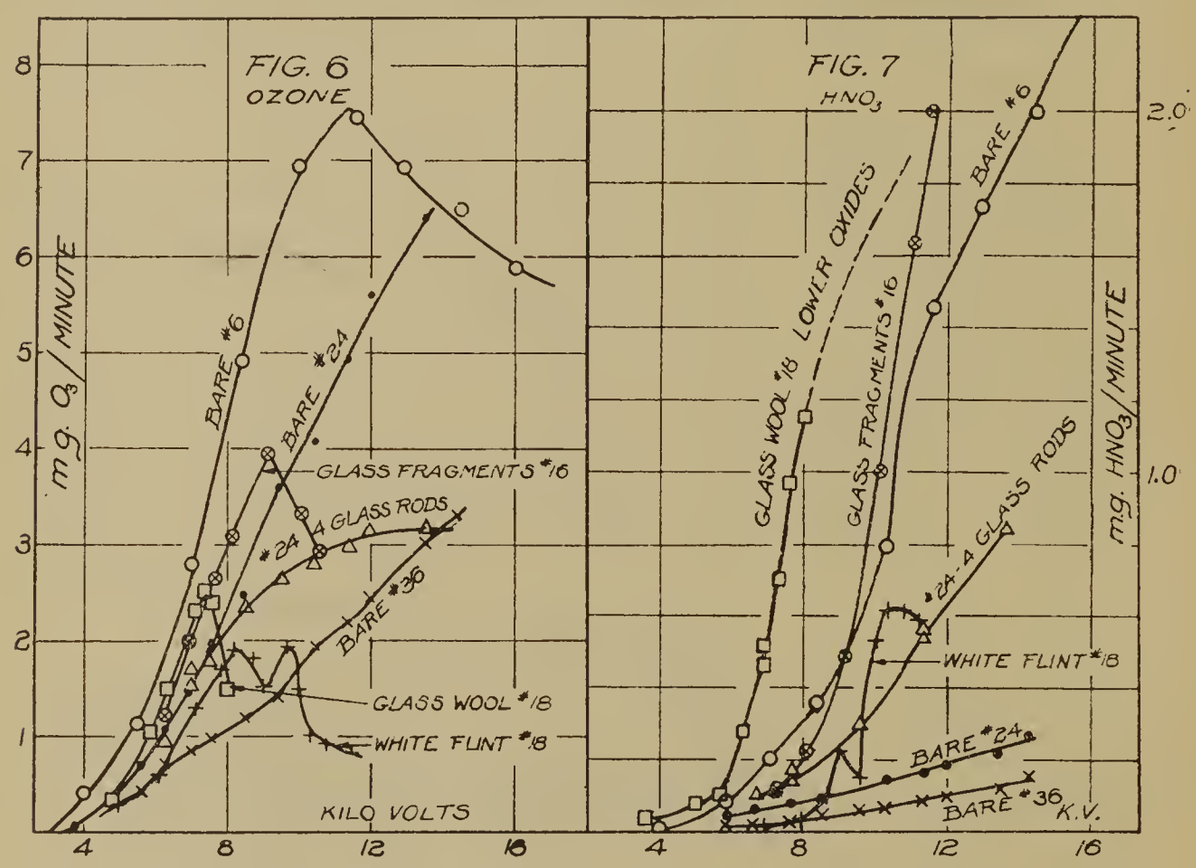

FIG. 6.—Gives yields of ozone and Fig. 7 gives the simultaneous yields of nitric acid in several Liebig condensers at a flow rate of 200 cc. per min.

there is an increase in electrical capacity, in the discharge current, in the brush character of the discharge, and in ozone and nitric acid formation, at voltages below their reversal points.

Four glass rods of 2 mm. diameter were placed concentrically with a No. 36 wire[19] and the results are included in Fig. 6 and 7 for flowing air. The following kinds of dielectric fragments have been used in experiments: ordinary soda-lime, pyrex and fused-

[18] Cf. Anderegg and Bowers. Proc. Indiana Acad. Sci. 1922. A Type of Silent Discharge Involving Catalysis.

[19] F O. Anderegg, *ibid.*, 1922. A Further Study of Pressure Reversals in the Corona Discharge.

silica glass, porcelain with and without impregnation with beeswax, white and blue flint, hematite, potassium chloride, and glass wool. All of these materials give the same general type of curves. Some of the results are plotted in Fig. 6, and 7. The weight of glass in the fragment tubes was about four times that in the wool tubes, but the ratio of surface to air volume was, on the other hand, about four times as great for glass wool.

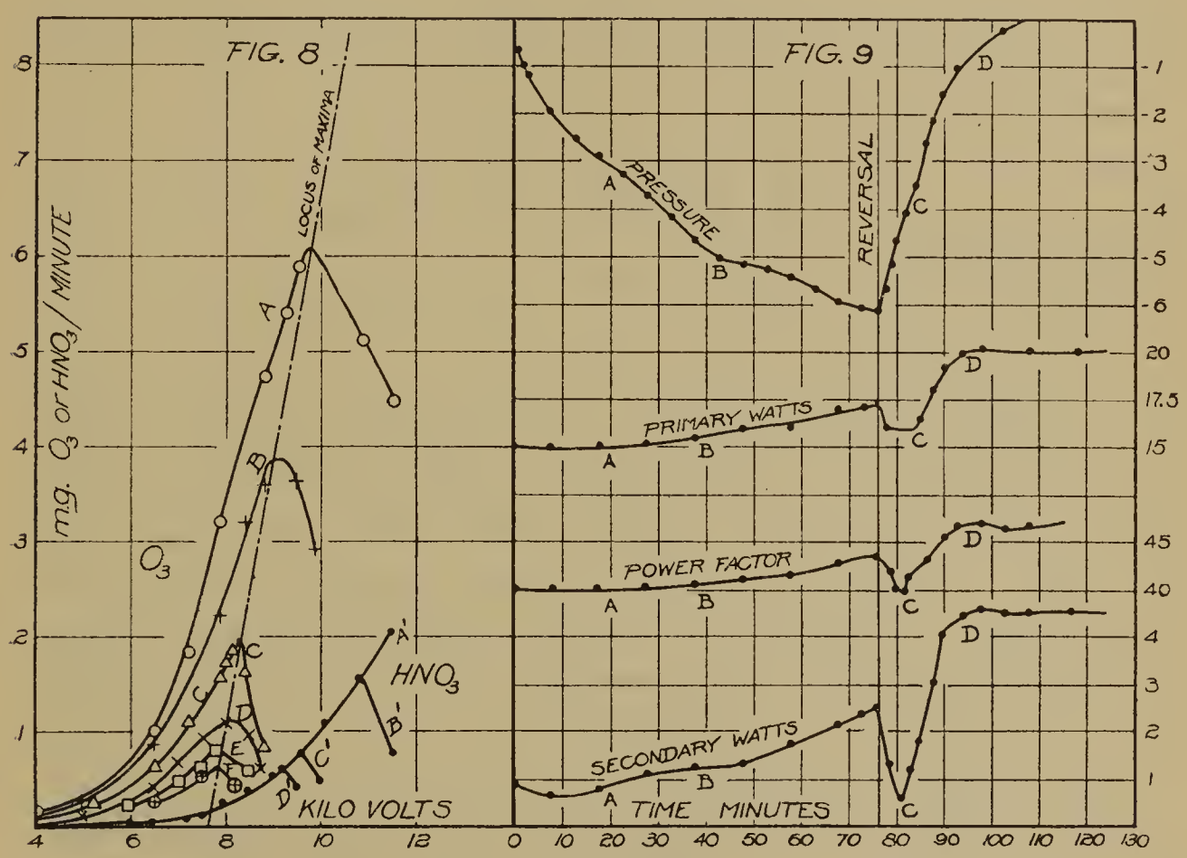

FIG. 8.—Gives the yields of ozone and nitric acid in a Liebig condenser with glass fragments packed around a No. 16 aluminum wire. The flow rates used were: A, A′, 1000 cc.; B, B′, 500 cc.; C, C′, 200 cc.; D, D′, 100 cc. E, 50 cc. and F, 25 cc. per min. The locus of the ozone maxima is a straight line. At lower voltages the nitric acid formed is constant within the experimental error, for all the flow rates used.

FIG. 9.—Gives the data for one of a large number of runs. The observed simultaneous changes in wattage, power factor and pressure aid in understanding the complicated chemical and adsorption reactions that take place in the discharge tube. Similar results were also obtained with air enclosed in Siemens ozonizers.

The remainder of the study was made with air enclosed within some of these same tubes, varying in duration from a few minutes to 72 hr. A discharge at 6400 v. was passed through air, enclosed in the tube containing glass fragments and a No. 6 wire. Fig. 9 gives the record of run 3, and similar changes in the curves were observed in all except run 4 of the 18 runs made with this

tube. The reversal time and the pressure decrease at reversal are given in Table I.

TABLE I.

Pressure Rerversal in the Corona Discharge.

A discharge at 6400 v. was passed through air enclosed in a Liebig condenser containing glass fragments and a 3.80 mm. aluminum wire.

Run	1	2	3	4	5	6	7	8	9
Min. to reversal	144.0	87.0	76.5	None	91.0	61.5	62.0	47.0	50.0
Pressure decrease, mm. Hg	9.4	6.7	6.1	Inc.	11.6	6.3	9.5	4.2	4.3
Run	10	11	12	13	14	15	16	17	18
Min.	54.0	47.0	46.5	55.0	58.0	51.5	45.0	72.0	55.0
Pressure decrease, mm. Hg	3.8	4.3	5.1	4.05	5.0	4.75	3.9	9.2	3.5

The tendency during these runs is toward a quicker reversal and a smaller pressure decrease. In run 4 the glass tube leading to the manometer was filled with air, which had been contaminated from a discharge in another tube, so that the pressure did not fall. A duplicate of this run with another tube gave the same results. In these two runs the wattage and power factor remained constant and the appearance was that of the discharge upon reaching a steady condition after reversal. No ozone was formed in these two runs.

Run 13 showed that a mixture of nitrogen and hydrogen standing in the tube for two weeks had no appreciable effect. Runs 5 and 7 gave evidence that passing steam through the outer jacket for two hours removed some of the material adsorbed on the glass, so that there was opportunity for greater pressure decrease during a comparatively short time. This process seemed to leave the surface in an activated condition. A similar effect was noted in run 17. This was caused by passing a discharge at 6400 v. through a mixture of nitrogen and hydrogen flowing through the tube. The smell of ammonia in the effluent gas was plain. An activation was indicated, similar to that secured by steaming.

A tube containing a No. 16 wire gave similar results at 8400 v. The discharge was passed through a mixture of nitrogen and hydrogen for 440 min. at 7500 v. A total decrease in pressure of 19

mm. Hg was noted; but analysis of the products showed the presence of only 0.01 mg. ammonia, whereas the pressure change indicated the formation of 190 times as much. The next run with air again gave a large pressure decrease, indicating an activated surface.

Glass wool was packed inside a Liebig condenser so that the apparent density of the contents of the tube was about 0.3; while the ratio of surface to air volume was 125. The large surface required a long time to become saturated, even at elevated voltages. Part of the substances which had accumulated to shorten the reversal time evaporated when the contents of this tube were removed, and allowed to stand above a radiator for one day. Repeated evacuation of long sweeping out with dry air was ineffective in removing these adsorbed substances, while one hour of steaming helped but little with so large a surface. White flint was found to have a remarkable adsorptive power so that a very long discharge was required to secure any reversal in pressure; but once saturated the reversal point was quickly reached. Fragments of pyrex glass were packed around a 3.8 mm. wire in a pyrex tube surrounded with a water jacket. The first run reached the reversal point in 75 min. at 10,000 v. with a pressure decrease of 6.0 mm. Repeating at the same voltage after sweeping out over night gave no pressure decrease. Run 3 at 8400 v., however, gave a reversal at 220 min. and 19.0 mm.

With small crystals of potassium chloride at 7500 v. the pressure fell during 25 hr. and at 13,500 v. for 10 hr. before a pressure reversal set in. The outside of the inner tube opposite empty spaces was spluttered.

A tube was filled with glass wool around a 3.8 mm. wire. Two distinct discharges were produced depending upon the length of time after the previous discharge. The first discharge and those which occurred after a rest of several days were of the "scintillation" type. This discharge appeared to creep out from the wire along individual fibers, which became so hot as to actually fuse, giving out a yellow light. On reaching the glass tube the discharge expanded, or apparently burst into multicolored fragments like fireworks. Fluctuations were observed in the current during the formation of these scintillations. In the yellow light

the spectrum was broken by absorption bands at more or less regular intervals. The D sodium lines were not observed.

The other type of discharge, which appeared in the tube after short periods of rest, is called the "glow" discharge. The tube was filled with a beautiful purple glow, which seemed to bathe the whole surface of the wool. Most of the experiments with this tube were carried out at about 12 kv. The spectrum consisted of a series of light and dark bands. Deposits of a yellow condensate on the inner surface of the tube were noted. Copious brown fumes were given off at times. The outer surface of the inner tube was badly spluttered at the ends of the glass wool.

DISCUSSION.

A study of the results indicates a complicated series of chemical reactions in the corona discharge, together with adsorption of some, at least, of the products on the surfaces. The following explanation offered for the variations in the curves plotted in Fig. 9 will explain most of the results obtained. At first ozone is formed[19] and then nitrogen pentoxide accumulates gradually. Heavy ions of low mobility[20] which decrease the conductivity are formed, explaining the first drop in wattage and power-factor curves. These heavy ions or molecules condense out on the walls with more or less lag to produce kinks[21] in the curves at A and B.

These adsorbed substances, containing probably heavy oxides of nitrogen which are quite polar, have a high dielectric constant, causing an increase in discharge density explaining the rise in power factor and wattage curves. Oxides then decompose the ozone,[19] so that when it decreases below a certain value the adsorption is less than the desorption and the pressure rises. Some of the heavy molecules evaporate, slowing up the speed of the ions and decreasing the conductivity, explaining the sharp drop in the power factor and other curves.

With the decomposition of the heavy ions at C there is another

[20] Daniels and Johnston, J. Am. Chem. Soc., **43**, 53, 72 (1921); H. B. Wahlin, Phys. Rev., **20**, 267 (1922). Hautefeuille and Chappius, Compt. rend. **92**, 80 (1881); Warburg and Leithaeuser, Ann. Physik., **23**, 209 (1907) and Ladenburg and Lehmann, *ibid*, **21**,—(1906) give evidence for the existence of a complex N_2O_5—O_3 compound.

[21] The examination of published data shows these kinks to be the rule; cf. cit. 14. R. H. George, private communication, working with different mixtures of oxygen and nitrogen, notices these kinks.

kink, from which the conductivity and pressure rise to a steady state at D, which was reached at 8400 v. in about 30 min. after reversal. Increases in temperature, in the intensity of the discharge or in the amounts of nitrogen oxides, contaminants from previous runs, will lower the ozone concentration and so speed up the reversal. Variations in results follow variation in the extent and in the degrees of saturation and of activation of the surface.

The postulate of Schuster[22] of an adsorbed layer of gas of high inductive capacity to explain the variations in sparking potentials for small gaps, would also help explain the changes in power factor either side of the reversal point. Such changes in specific inductive capacity with adsorption and desorption, bring about changes in potential distribution across the tube. The change in the character of the discharge, from the glow comparatively of low potential gradient to the intense streamers of higher grade discharge that accompanies these changes, is evidence for this hypothesis.

Another possible source of complication lies in the spluttering action[23] of the discharge, see Fig. 1, 2 and 3. In these experiments spluttering of glass and other material has been observed. Even when not directly visible there is always a considerable possibility that this action is occurring in sufficient amount to affect the results.

From the experiments described we may conclude that the choice of material, of which to make a discharge tube for the quantitative study of chemical reactions in the corona discharge, is very important. It might seem that no material could be relied upon not to complicate the reactions until extensively tested. The use of a dielectric such as glass to intensify the discharge is apt to cause complications, not only because of adsorption that may occur, but because of the probable existence of progressive changes within the dielectric under stress.[24]

In acknowledgment for valuable assistance in obtaining these

[22] A. Schuster, Phil. Mag., **29**, 197 (1890).

[23] J. J. Thomson, Conduction of Electricity through Gases, 1st Ed., p. 451. A. Goetz, Physik. Z., **23**, 126 (1922). Research Staff of the General Electric Co. Ltd., Phil. Mag., **45**, 98 (1923).

[24] W. D. Peaslee, Trans. Am. Inst. Elec. Eng., **36**, 527 (1917).

results, thanks are due to Messrs. W. H. Herr and O. F. McIlvaine.

DISCUSSION.

F. E. HARTMAN[1]: We have found that when both electrodes are straight, and consequently parallel at all points, there is a marked tendency for the discharge to intensify at the edge of the inner electrode, and the dielectric will ultimately rupture at this point. On the other hand, we have found that by drawing out the central electrode in such a way as to form the frustum of a cone, and thus produce a gradually increasing space between the ends of edges of the electrodes, we could succeed in eliminating the intensified discharge, and in consequence remove the liability of dielectric rupture. We have not given this phenomenon any theoretical consideration, but have attributed the rupture to local high temperatures, produced by the intensified discharge. The elevated temperature decreases the dielectric material, and thus permits the perforation tension to be reached.

The tendency of a discharge to creep is marked whenever point-on-edge discharges are used. When the polar space is gradually increased an edge is avoided and the field of flux is maintained uniform at all points on the discharge surface, and dies off gradually as the polar distance is gradually increased. Has any one here given this point sufficient consideration either to confirm or to contradict our opinions?

K. B. MCEACHRON[2]: I think the answer found by Mr. Hartman is the correct solution. In the design of the high tension transformer bushing this question plays an important part, and it is one of the fundamental rules that the design must be so arranged that the concentration of stress at any one point is prevented. Mr. Hartman might have obtained exactly the same result by increasing the diameter of the outer tube at the ends, so that the stress per unit area does not exceed a proper value. In any case, it is necessary to prevent the formation of sharp edges, or anything approximating a sharp edge, in order that the concentration of flux will not break down the dielectric.

[1] United States Ozone Co., Scottdale, Pa.
[2] Lightning Arrester Eng. Dept., General Elec. Co., Pittsfield, Mass.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Colin G. Fink in the Chair.

THE INFLUENCE OF THE SHAPE OF THE CATHODE ON THE NORMAL CURRENT DENSITY OF THE GLOW DISCHARGE.[1]

By A. Guenther-Schulze.[2]

Abstract.

Experiments on the normal current density of the glow discharge with a U-shaped cathode in hydrogen have shown that, if the pressure of the gas is of the right magnitude, the normal current density between the arms of the cathode may be eleven times that at a flat cathode. The thickness of the dark space decreases as the two arms are made to approach each other. These phenomena occur if the arms are so near each other that the electrons emitted from each arm penetrate the dark space of the other. These penetrating electrons, if they are moving with sufficient velocity, will produce ions in the dark space, and so the two arms will increase each other's current densities.

[D. MacR.]

The following experiments were performed to determine the effect of the shape of the cathode on the normal current density of the glow discharge.

1. One (k) of two similar iron sheets 0.5x15x 100 mm. was bent as shown in Fig. 1, while the other (1) was used flat. They were sealed into a glass tube, the one as anode and the other as cathode. The current direction could be changed by a reversing switch. Then for a number of different hydrogen pressures the current strengths were determined at which the plates were just completely surrounded by the glow discharge. The measurement gave the results shown in Table I.

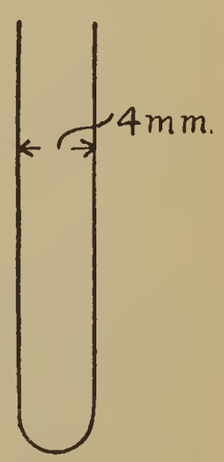

Fig. 1

[1] Manuscript received August 21, 1923, Translated by Duncan MacRae.
[2] Physikalisch-Technischen Reichsanstalt, Berlin, Germany.

TABLE I.

Expt. No.	Pressure mm. Hg	i_l Milliamp.	i_k Milliamp.	i_k/i_l
1	0.735	1.47	0.76	0.517
2	1.19	4.04	2.75	0.618
3	2.27	14.1	84.3	5.98
4	3.29	30.0	66.3	2.21
5	4.15	47.9	69.3	1.45
6	4.76	62.7	75.0	1.20
7	6.63	121.5	94.0	0.773
8	7.88	172.0	99.5	0.579

In Fig. 2, the values of Table I are plotted. In experiment 1 the normal current strength for the bent sheet is half that for the straight one, as was to be expected, since the gas pressure is so small. Consequently the length of the dark space is so great that there is no discharge possible between the arms of the bent sheet. However, as soon as the pressure rises high enough for the discharge to penetrate the intermediate space, the current density increases quite astonishingly. Insofar as it does not change on the outside of the sheet, the ratio of the current density in the space between the arms of the bent sheet to that on the straight sheet is as follows, using values of experiment 3:

$$\frac{84.3 - 7.05}{14.1 - 7.05} = 10.95$$

In experiments 7 and 8 at the higher pressures, and with the glow lying close to the electrode, the current strength on the bent sheet again becomes smaller than on the straight one, owing to the fact that the current at higher pressures encounters a much higher resistance in the narrow slit of the bent sheet than it does with the straight sheet, which is freely accessible from all sides. At a critical pressure of about 2.25 mm. the current strength varies regularly between 13 and 80 milliamp.; at the high current strength of 80 milliamp. the sheet and the space between its arms are so strongly heated that the gas density decreases until the dark space no longer exists in the slit. The glow discharge disappears, the current falls to 13 milliamp., the sheet cools down until the discharge can again jump into the slit, and so forth.

By means of this phenomenon the cathode may be heated very strongly. If, for example, a cathode of a spirally wound strip is used, it can be heated bright red without having to materially exceed the voltage of the normal cathode fall. If two platinum dishes, placed one within the other under a receiver, with a rather small space between them and with the outer one sur-

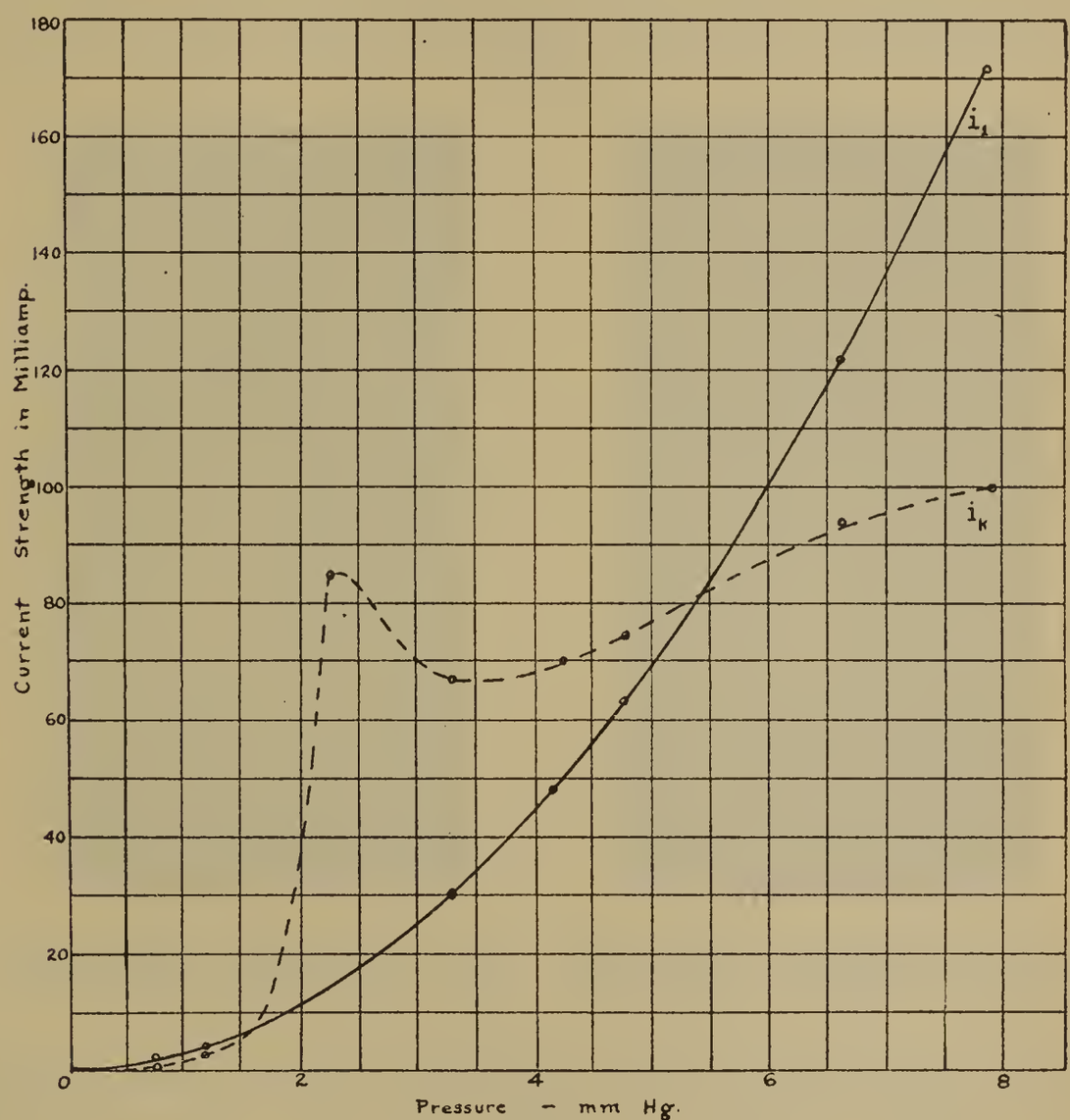

FIG. 2

rounded by a heat insulator, are made the electrodes of a glow discharge, incandescent temperatures can easily be attained. By this means any convenient salt, as desired, may be heated or melted in an atmosphere of hydrogen, oxygen, argon, etc.

A marked decrease in the thickness of the dark space occurs simultaneously with the entrance of the glow into the slit. If the current strength is reduced to less than normal, the discharge

vanishes at first on the outside of the bent plate; and only after it has been completely extinguished there, and after considerable further decrease in current density has taken place, does it disappear within. From this it may be concluded that the normal cathode fall is less from within than without.

2. In order to investigate conveniently how the increase of current density and the decrease in thickness of the cathode fall region depends on the distance between the two arms of the bent

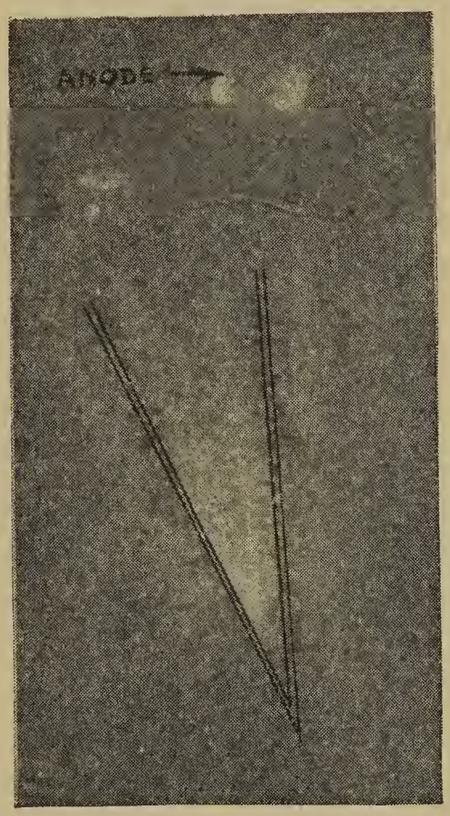

FIG. 3. Hydrogen at 0.83 mm. pressure. i = 27 milliamp. Cathode just completely covered by the discharge.

FIG. 4. Hydrogen at 0.95 mm. pressure. i = 6.5 milliamp. Cathode only partially covered by the discharge.

sheet, an iron sheet was bent in a V-shape so that the two straight arms formed an angle of 25° with each other. The anode was placed above the sheet. Again the current strength in hydrogen was increased until the sheet was just covered all around with the glow discharge. Fig. 3 represents the phenomenon under these conditions. It shows at once that (a) the glow more nearly approaches the cathode surface the closer the arms come together until a minimum distance is reached, and shortly thereafter bends back towards the other arm. (b) the brightness, as well as the current density of the glow becomes greater the more nearly it approaches

the cathode. In Fig. 5, the thickness of the dark space as a function of the distance from the vertex of the angle between the arms is plotted on a large scale. The figure shows that the thickness of the dark space rises from the minimum, which only amounts to a full third of the normal thickness, at a rate approximately proportional to the distance from the vertex of the angle, until it has attained the normal thickness. When the distance has become four times the normal dark space thickness, the opposite arm has no longer any effect. Accordingly it appears that: (c) the

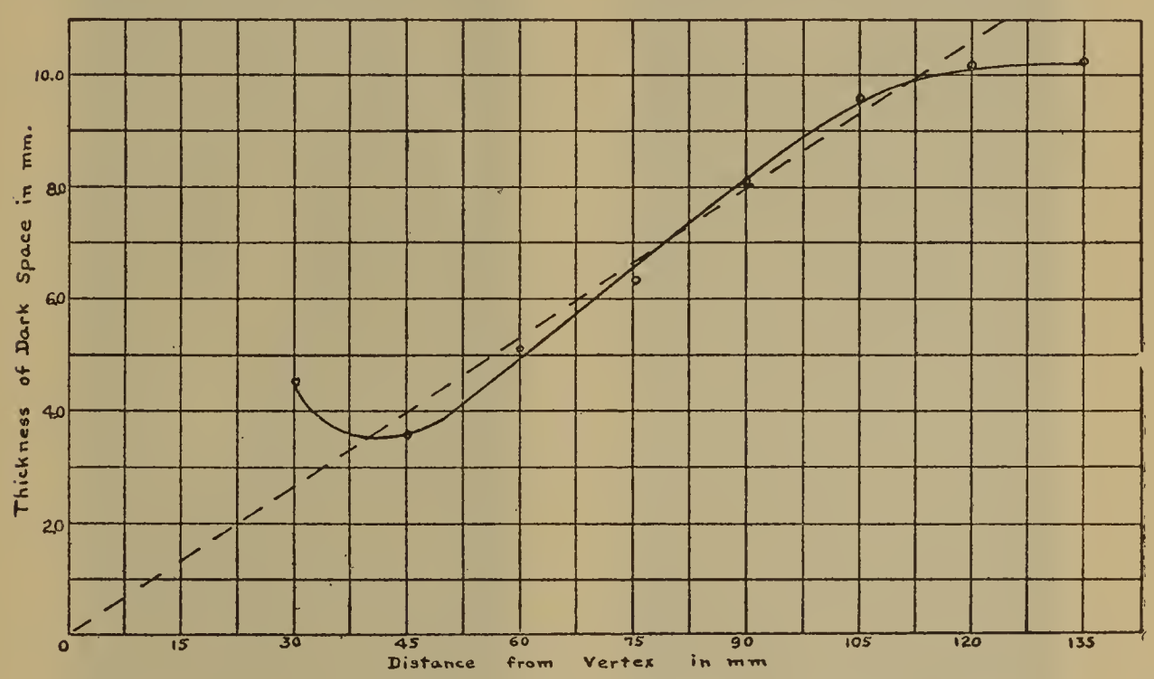

FIG. 5.

decrease of the thickness of the dark space is inversely proportional to the distance between the two cathode arms. It further appears from the experiments that: (d) the phenomenon occurs also in air, (e) the phenomenon exists also in the field of the abnormal cathode fall, for example at current densities sixteen times the normal.

If the current strength is decreased below the normal, the glow draws together into a kind of an ellipse as shown in Fig. 4 and vanishes completely outside. The bright light outside the arms in Fig. 4 is part of the glow extending in front of and behind the ellipse.

3. The inside of one arm of the V-shaped sheet was covered with a thin mica sheet. Fig. 6 shows that then the effect com-

pletely vanishes. The glow runs at a constant distance from the cathode, until it strikes bluntly against the mica covered arm. The density is the same over all.

4. Investigations were carried out to determine how the observed phenomenon of the shortening of the dark space, and the simultaneous increase of current density, depend on the angle which the two arms of the sheet make with each other. The experiments were performed in air at a pressure of 0.25 mm.

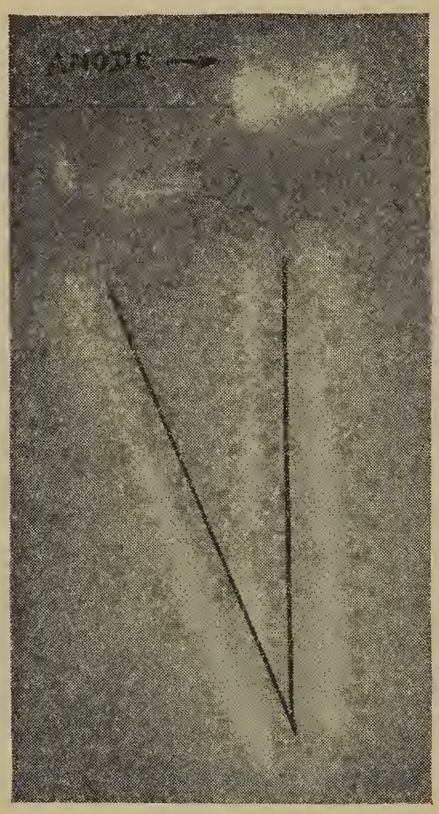

Fig. 6. Air at 0.50 mm. pressure. i = 11.5 milliamp. The inner side of left arm covered with mica.

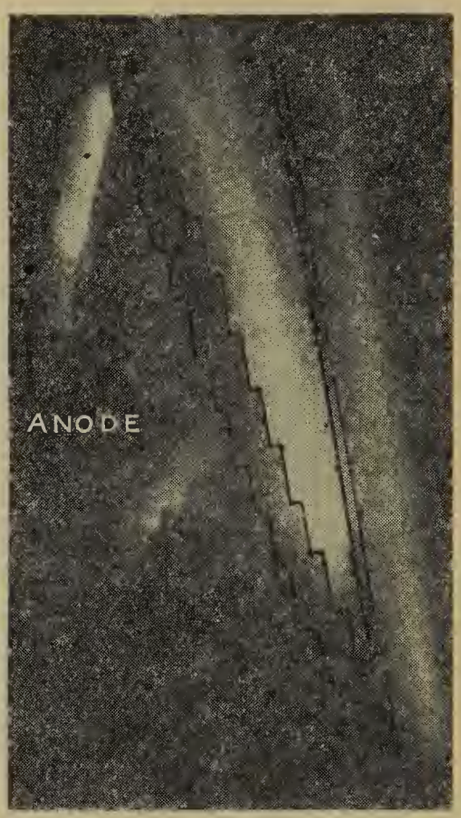

Fig. 8. Air at 0.20 mm. pressure. Cathode not quite completely covered by discharge.

with a sheet 3 cm. broad and with 8 cm. arms. The arms were at first usually bent so as to be at an angle of 90°. Fig. 7a and 7b show the results. At an angle of 80° no action of the arms on each other could be determined. Then it increased rapidly with decreasing angle until at small angles it again became nearly constant.

5. In order to be able to investigate the influence of the distance between the arms at an angle of 0° one arm was made in step form as shown in Fig. 8. Table II gives the results obtained.

Table II shows that here, as also in experiment 4, the phenomenon in hydrogen is considerably more strongly marked than in air.

While in air the thickness of the dark space decreases from 10.0 to 3.0 mm. and thus to 30 per cent of its original value, in hydrogen the thickness of the dark space recedes to 15 per cent. Furthermore the decrease of thickness begins in air as soon as the angle in air has approached two times the dark space thickness, and in hydrogen at four times the dark space thickness. As the dark space decreases, the current density increases.

TABLE II.

Distance Between The Arms in mm.	Thickness of the Dark Space		
	In air at 0.215 mm. Pressure at Normal Current Density mm.	In Hydrogen of 1.00 mm. Pressure	
		At Normal Current Density mm.	At Strongly Abnormal Current Density mm.
25	...	9.4	7.4
23.2	10.0	8.6	6.2
20.7	10.0	7.6	5.4
18.3	9.0	6.6	4.8
15.7	8.0	5.8	4.4
14.3	7.0	4.8	3.4
12.6	6.7	3.8	2.6
10.7	5.3	3.2	1.6
8.7	4.0	2.6	0.6
6.7	3.0	2.0	0.4
4.7	...	1.4	0.2

6. From the foregoing it seems to follow that tube shaped cathodes would show the phenomenon markedly. For example in hydrogen, an iron tube of 1 mm. wall thickness, 3 cm. outside diameter and 3 cm. length showed simultaneously a dark space of 4.1 mm. thickness within and one of 12.5 mm. without, while the current density within amounted to many times that of the outside.

AN EXPLANATORY EXPERIMENT.

Two causes are conceivable to acount for the strong increase of the normal current density, as repeatedly portrayed in the foregoing experiments, and for the decrease of the dark space thickness by the mutual influence of the parts of a glow discharge. These causes are: first, the electrons emitted by the cathode and, second, the radiation of the glow. Now experiment No. 4 shows, well

enough, that the radiation cannot be the cause of the phenomenon, for with increase of current density as a result of mutual radiation of the cathode surfaces, it would be difficult to understand why the effect has completely vanished at an angle of 80°. Consequently we attribute the phenomena to the electrons.

In order to consider the action or effect of the electrons let us choose the simplest case—two parallel cathode arms facing each other at a small distance apart as in Fig. 1. In this case (a) each surface hinders the heat radiation of the other. The two arms, and consequently also the gas between them, become hotter than if the

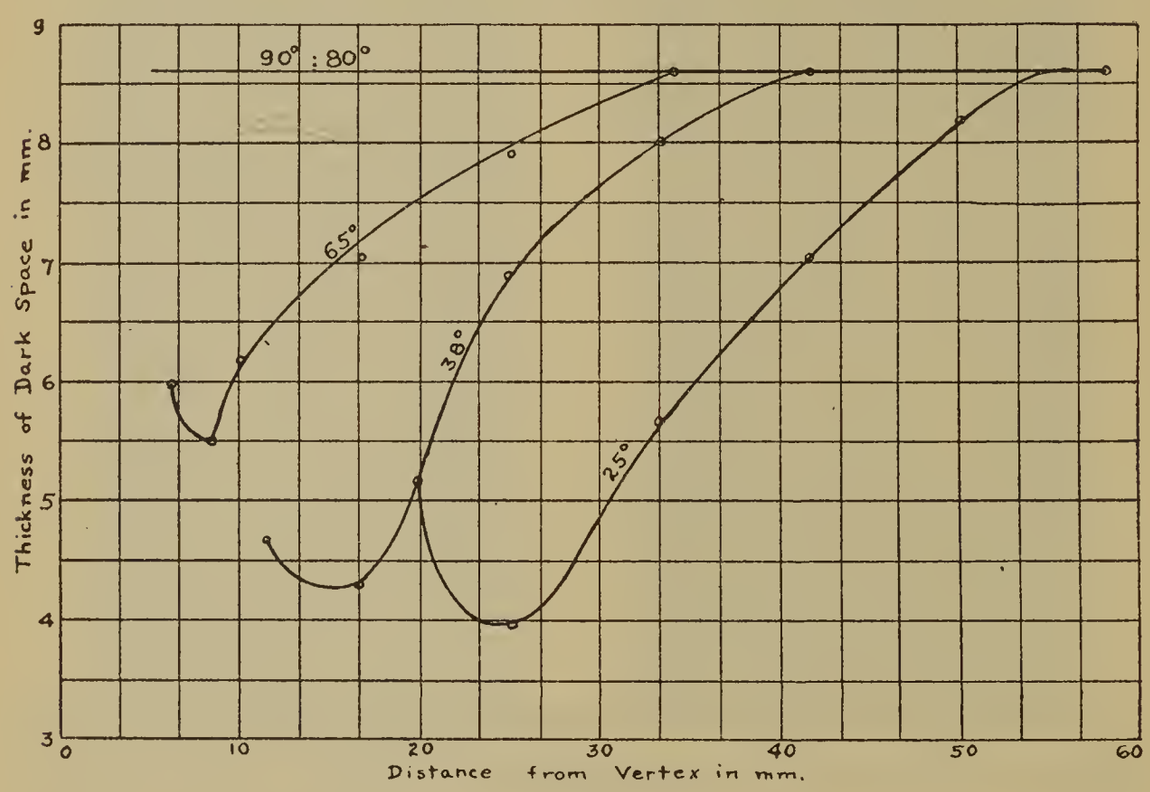

FIG. 7-a

sheet were plane. Thus the normal current density between the arms of the bent sheet ought to be less than on the straight sheet. (b) the path of the discharge to the inner side of the bent sheet is longer and narrower than to the outside. Therefore the current density ought to be greater outside than within, instead of the reverse. (c) If the zones of the glow partly overlap, the ion concentration in the common field is greater than if each glow existed separately. The combination of ions increases with the square of the ion concentration. Thus the combination of ions between the sheets ought to be greater and therefore the current density ought to be less than outside. Thus all three considerations lead

to conclusions as to the behavior of the discharge contrary to what was actually observed.

Perhaps experiment No. 4 gives further light on this point. According to this the phenomenon occurs if the arms are so near to each other that electrons emitted from each arm penetrate the dark space of the other arm, and the effect is the more pronounced the deeper they penetrate. Furthermore, it folows from the experiments that these electrons proceed from the cathode to the end of their path mostly in straight lines at right angles to the cathode. For, if a substantial part of them were to suffer rather large deflections, without thereby losing their velocities, the effect would have to be present even at an angle of 80° between the arms.

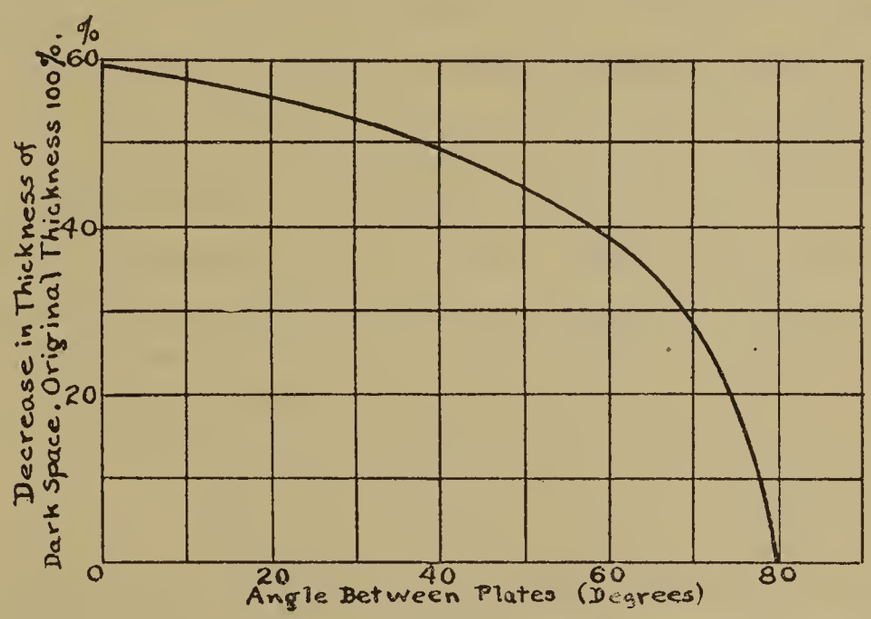

FIG. 7-b

However, the fact that the electrons penetrate the opposite dark space and there produce ionization still does not explain by itself the rise of the current density. Let us assume that at a plane cathode each of its outgoing electrons after passing through the normal cathode fall attains the ability to produce n ionizations. If now the two arms approach sufficiently near to each other, the part $x\ n$ of the n ionizations lying on one side of the "potential boundary" are effective for the inner arm and the part $(1 - x)\ n$ lying on the other side are effective for the opposite arm. Then there are as before n cations available for each arm.

As a further help in interpreting our experimental results let us consider the combination of ions. At a plane cathode probably

most of the ionization takes place in the glow. Now since in the glow the field strength is very small and the ion concentration great, the combination of ions is also proportionately great, and only a fraction of the cations produced arrived at the cathode through the dark space and are able to set free electrons there. The "efficiency" of the ionization is much less than 100 per cent.

However, if the two arms of the sheet are brought together so close that the electrons of the one arm penetrate into the dark space of the opposite arm at velocities a good deal above the ionization velocities, these electrons will move against the field, their velocities will shortly be reduced to zero, and they will then pass back into the glow discharge area. However, the cations resulting from the passage of the electrons through the dark space persist, since on account of the high field strength in the dark space little recombination takes place. The efficiency of ionization in the dark space is nearly 100 per cent. On this account more cations are at the disposal of the opposite arms than before. These produce more electrons, these again more cations in the dark space of the first arm and thus the two arms increase each other's current densities, until the increasing combinations of ions in the glow and the rising temperature of the gas and of the electrode arms lead to equilibrium. As Fig. 2 shows, this sometimes becomes the case when the current density has risen to a 11-fold value.

The decrease in thickness of the dark space associated with the increase of current density may have the same causes as the quite analogous phenomenon in the field of abnormal cathode fall. Apparently, with a given gas density and cathode material the current density and the thickness of the dark space are closely related to each other, and it is immaterial whether the cathode fall is great, as in the abnormal field, or small, as in this case with the mutual influnce of surfaces turned towards each other. For, on increasing the current density by the mutual influence of the two arms the cathode fall initially appears not only *not* to rise, but to fall. The final decision of this question, which seems to carry us into the complex field of the normal cathode fall, must be reserved for a future special investigation.

TRANSLATOR'S NOTE—Responsibility for inaccuracies in translation of this article are assumed by the translator, Duncan MacRae.

DISCUSSION.*

C. G. SMITH[1] (*Communicated*): The experiments of Dr. Guenther-Schulze are interesting and convincing. An addition to or confirmation of the theory of the striking phenomena observed can be made in the light of certain observations made by Dr. Vannevar Bush and myself.

In experiments on the glow discharge between concentric cylinders, a great change of cathode dark space can be produced under proper conditions by the application of a magnetic field with lines of force parallel to the axis of the cylinders. The magnetic field decreases the dark space. The field increases the probability for production of positive ions near the cathode. The observed total voltage drop between aluminum electrodes in helium at 2 mm. pressure was about 120 v. This is lower by 25 v. than the ordinarily observed normal cathode fall. The bent and cylindrical cathodes used by Dr. Guenther-Schulze likewise increase the probability for ion production near the cathode surface.

I think, however, the recombination phenomenon, to which he attributes his results, may be only one of the smaller factors, because in the parallel case of the magnetic field cited above, recombination was, under the conditions, a negligible factor. The distribution of positive space charge in and near the cathode dark space is, I believe, a more powerful factor in determining the current. When more positive ions are produced in the dark space, then the region where positive ions are densest is moved closer to the cathode surface. This has the effect of greatly increasing the number of positive ions per second that can be drawn up to the cathode surface for a given voltage drop. Hence the observed current is greatly increased.

It may be possible, in a careful analysis of the function of the positive space charge, to account for Dr. Guenther-Schulze's observations on the relative effects of air and hydrogen when used

* In the absence of the author the above paper was presented by Duncan MacRae.

[1] American Appliance Co., Cambridge, Mass.

with his bent cathodes, the great difference in weight of the positive ions of air and those of hydrogen being an important factor. However, the analysis requires the taking into account of many factors and is undoubtedly difficult. The experiments with the bent cathodes nevertheless are illuminating, and lead us nearer to a complete understanding of the cathode fall of potential.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

RECENT PROGRESS IN THE PRODUCTION OF OZONE WITH HIGH TENSION DISCHARGES.[1]

By Frank E. Hartman.[2]

Abstract.

This paper deals with the production of ozone by the so-called silent discharge. Data are given which show that the energy density of an ozonizer is a straight line function of the cycles; and that the yield of ozone is a straight line function of the energy density, at atmospheric pressure. It is further shown that ozonizing at high gas pressures is conducive to better cooling of the electrodes, thus making it possible to produce high concentrations of ozone with high energy densities. A relationship is also established between high gas pressures and the efficiency of an ozonizer.

The value of an oxidizing agent that produces no contaminating residue is so thoroughly realized in chemical circles that ozone investigations excite unfailing interest. The obstacle in the path of the more general adoption of ozone by the industries is not found so much in the cost of ozone on the pound basis, as it is in the cost of apparatus capable of continuously producing ozone in quantities demanded for commercial uses.

The production of ozone is governed by the general laws of physics. In calculating the efficiency of an ozone generator, the procedure would not differ essentially from that involved in calculating the efficiency of an electric motor. Power obtained over power input determines the efficiency of an ozonizer and a steam engine alike.

Considering 34,000 cal. as the heat of formation of ozone, the

[1] Manuscript received June 20, 1923.

[2] United States Ozone Co., Scottdale, Pa.

theoretical yield of an ozonizer is 1.2 kilos per kw-hr. Calculating this against the advertised data of reliable manufacturers of ozone apparatus, we find, at the concentrations more generally demanded by the industries, that industrial ozonizers attain an efficiency of approximately 15 per cent in oxygen and 5 per cent in air.

The enormous advantage that ozone offers in many chemical reactions not only permits, but actually recommends, its use on the basis of production cost, regardless of the above low efficiencies. When one considers these facts, one is led to ponder on the present sparing use of ozone in the manufacture of fine chemicals. This question is at once answered by the relatively high first cost of ozone apparatus.

There is, of course, a reason for the wide difference that exists between the production and apparatus cost of ozone. The yield of ozone per generating unit is dependent upon the velocity of the gas being ozonized, and the energy density occasioned by the generator. In ozonizers, the energy density is notoriously low. For instance, a standard ozone generator as manufactured in our factory for water purifying machines of small capacity has a total anode surface of 400 square inches. This generator, when operating under optimum conditions, absorbs 200 watts, or operates with an energy density of 0.5 w. per sq. in. This generator retails at $100 per unit. In order to produce one pound of ozone an hour with these units, thirty-seven of them would be required, when operating at concentrations demanded by most industrial processes.

From the point of view of a manufactured product, these units are satisfactory. Their operating cost is satisfactory to the chemical industries, but the investment of $3700 in order to produce a pound of ozone per hour absolutely limits their application where large quantities of ozone are required. The writer arrived at this point of his consideration several years ago. In seeking further advances, the only course seemed along avenues that offered more ozone from existing generators. This was rather a Hobson's choice; since avenues already opened up through efforts to build new generators were so numerous as to throw one into a quandary for something original.

Increasing the potential difference between the electrodes of an

ozonizer will increase the energy density, but due to the necessity of a solid dielectric in our type of generator, there was a decided limit to which the potential could be increased. Polar distances, etc., showed some relation to the ozone yield, but their influence was infinitesimal, and we sought something enormous.

A further consideration of the circuit of an ozone generator reveals that its only resistance is a capacity resistance (Fig. 1). Capacity resistances are proportionate to $1/2\pi fC$, where f = frequency and C = capacity. Experiment has established that capacity is little affected even by exceedingly wide changes in frequency. From this, it follows that the resistance of ozone circuits is inversely proportionate to the frequency. From Ohm's law, we know that the current flowing through a circuit is inversely proportionate to the resistance. The sum of these facts reveals that the energy density of an ozone circuit is directly proportionate to the frequency.

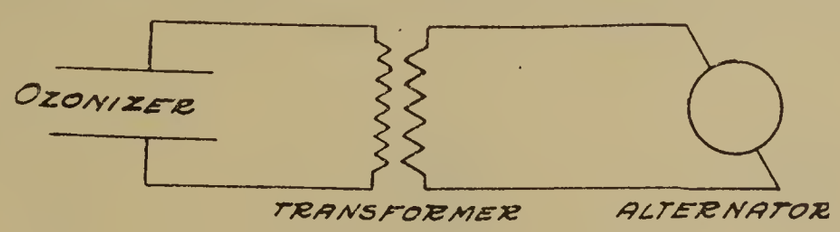

FIG. 1.

I have used throughout the term "energy density," since it is well established that the production of ozone is not accomplished through a sort of gaseous electrolysis of oxygen or oxygen mixtures, and is not, therefore, dependent upon current density. In fact, the relationship between the production of ozone, the current density and the potential difference have never been sufficiently established to permit the drawing of conclusions. We do know, however, that the production of ozone is a function of the total energy input. Warburg and Gray have obtained yields of ozone that correspond to 0.260 g. per coulomb, while if this were a true electrolytic reaction, only 0.0005 g. per coulomb could be formed.

Here we apparently possess a means of increasing the energy density of existing ozone generators, and thus increase their yield of ozone per unit of time. A search of the literature revealed that many workers had experimented with high frequencies, and

many patents had been issued covering high frequency ozonizers. The early workers had, however, employed damped waves, since at that time sustained waves of high frequencies were not available. The small available energy from damped waves renders them out of consideration in industrial applications. The advent of the radio telephone brought into existence high frequency alternators that produced sustained waves. Their earliest application to the production of ozone was made in 1914 by Puschin and Kauchtschev.[3] Their work tended to reveal a connection between the frequency employed and the applied potential. In this instance, they cite the following as essential to equivalent yields:

Frequency	Potential
1240	6500
950	7000
660	8000

An arbitrary calculation based on good ozonizer practice, reveals that the energy density would stand in the following relation:

Frequency	Potential	Watts per tube
1240	6500	32
950	7000	29
660	8000	25

The wattage figures are in sufficiently close agreement to indicate that its influence is probably the controlling one. One must always consider the other factors which enter. Puschin and Kauchtschev's report did not contain the data for estimating the extent to which they may have influenced results. Our work indicates that potential, taken separately, is with difficulty linked with ozone yield, while energy density is strongly linked. The work of the Russian investigators further points out that for a constant air flow an increase in frequency above 1240 cycles tends to decrease the ozone yield, while an increasing air flow displaces the maximum toward increasing frequencies.

During the year of 1919, I experimented with an alternator producing undamped waves having frequencies up to 1100 cycles. By using speed control and special transformers, I could work with cycles of 300, 500, 800 and 1100, and maintain the same potential

[3] J. Russ. Phys. Chem. Soc., 46, 576 (1914).

on the electrodes. At the time of these experiments, I was not equipped to measure the energy very accurately, so this factor was neglected and only the yield per generator was determined. Fig. 2 shows graphically the results of these experiments. At 60 cycles, this generator produced about 1 g. ozone per hr., and at

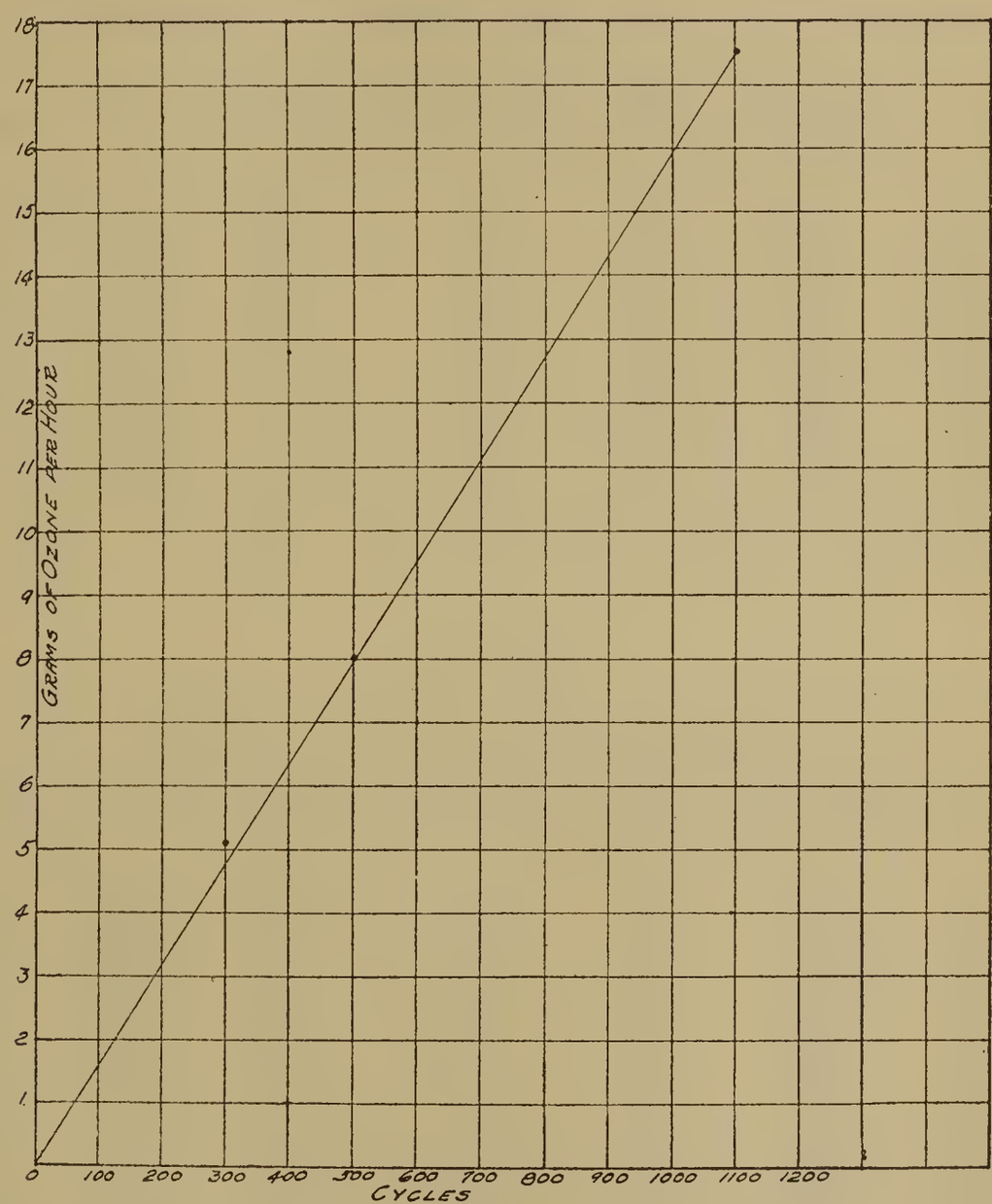

FIG. 2

1100 cycles, the yield was increased 17 times. Theoretically, I should have obtained an increase of 20 times, so such results were indeed gratifying. The ozonizer employed was not constructed for artificial cooling, and as the heat increased rapidly, I was forced to use exceedingly high air flows in order to obtain the maximum yields. This was detrimental to the concentration

of ozone, and in view of Puschin and Kauchtchev's work, I commenced to see obstacles ahead.

At that time, high frequency alternators were expensive, and

TABLE I.*

Production of Ozone with High Frequency Undamped Waves.

Frequency	Absorption of energy of the tube, w.	Energy yield g./kw.	Ozone concentration g./cu. m.	Ozone yield per tube per hour, g.	Tension v.	Nature of gas
50	2.12	134	21.3	0.285	5480	Oxygen
480	22.07	135	21.1	2.98	5830	Oxygen
770	31.9	135	22.5	4.31	5850	Oxygen
1080	44.2	130	23.0	5.73	5850	Oxygen
2510	118.7	138	20.7	16.4	5850	Oxygen
4810	207.0	138	22.7	28.6	5850	Oxygen
6880	303.0	146	20.5	44.5	5850	Oxygen
7900	348.0	142	19.7	49.4	5850	Oxygen
10020	415.0	139	22.6	57.7	5830	Oxygen

* Reproduced from Dr. Alfred Starke's thesis (1922).

TABLE II.

Production of Ozone with High Frequency Undamped Waves.

Frequency	Absorption of energy of the tube, w.	Energy yield g./kw.	Ozone contration g/cu. m.	Ozone yield per tube per hour, g.	Tension v.	Nature of the gas
50	1.97	48	6.3	0.095	5830	Air
410	16.3	51	6.1	0.831	5830	Air
980	41.5	46	5.9	1.91	5850	Air
1910	82.7	49	6.2	4.06	5840	Air
2780	119.8	50	5.7	5.98	5840	Air
3520	152.1	53	6.4	8.06	5850	Air
4650	198.0	48	5.3	9.50	5850	Air
5260	219.0	47	6.0	10.30	5830	Air
6010	248.0	51	6.2	12.65	5850	Air
6970	284.0	49	5.8	13.91	5850	Air
7930	315.0	47	6.4	14.80	5850	Air
8980	350.0	52	6.1	18.20	5850	Air
10030	389.0	49	5.8	19.10	5850	Air

not completely out of their experimental stage. These conditions, together, with the presence of other work, caused us to abandon high frequency experiments for a time. In 1922, Alfred Starke presented for his Doctor's degree at the Technical Institute of

Danzig a very interesting thesis[4] on the production of ozone with high frequency undamped waves. Starke completed his work under Prof. Hans von Wartenburg, who was for years in close association with Warburg and Nernst, so a fund of highly trained experience was available to him. The thesis contained many

TABLE III.

Oxygen Figures From Table I.

Frequency	Theoretical increase over 50 cycles		Observed increase over 50 cycles	
	Watts	Ozone	Watts	Ozone
4810	98	98	98	100
10020	200	200	196	202
Air Figures From Table II.				
5260	111	111	111	108
10030	201	201	197	201

TABLE IV.

Relation of Air Flow to Frequency.

Frequency	Nature of Gas	Velocity of gas, L. P. M.
50	Oxygen	0.223
4810	Oxygen	21.000
10020	Oxygen	42.500
50	Air	0.25
5260	Air	28.5
10030	Air	52.0

interesting observations on the structural features of ozonizers, together with the quantitative data of his experiments. Tables I and II are a digest of his results. As Dr. Starke is now a member of our research staff, we are printing an English translation of his thesis, and this will be furnished to those interested in the details of his work.

[4] A copy of the translation of this thesis will be supplied by the United States Ozone Co., Scottdale, Pa., upon request.

Referring to Table III, we find that Starke has been able to realize the theoretical increase in watts, and even better than the theoretical increase in ozone yield per tube. Referring to Table IV, we find that Starke's work serves to confirm the findings of Puschin and Kauchtschev, in that an increasing air flow is essential with increased frequency in order to obtain equivalent efficiencies. This is an annoying fact, since it demonstrates that high frequency alone is incapable of yielding high concentrations at an economic efficiency, and this is one of the offices so sought for in efforts to better industrial ozonizers. Without high concentrations of ozone, many volatile substances which react splendidly with ozone cannot be ozonized on a commercial scale.

The necessity of increased air flow with increased frequency is a direct result of increased energy. We have already seen that 85 to 95 per cent of the energy is lost in heat, so an energy increase of 200 times must, in the average size tube, be productive of very high temperatures at gas flows of less than a liter per minute. Thermal decomposition undoubtedly explains this. The gases, being such poor conductors of heat, cannot be efficiently cooled in the generator by economic means of artificial cooling.

The relationship between energy density and ozone yield has been strongly linked up to the present. Apparently an ozone generator is a highly inefficient apparatus for energy transmutation. To better its efficiency, one must go further afield, and the more advanced ideas of physical chemistry point to ionization. Rideal[5] commenting on Puschin, etc., advances three interesting steps on the formation of ozone, in the course of his explanation of the increased yield with increased frequency. Briefly, they are:

a. A splitting of the molecule into two neutral atoms:

$$O_2 = O + O$$

b. An ionization of the molecule or atom by impact:

$$O_2 \rightarrow O^+_2 + \ominus$$
$$O \rightarrow O^+ + \ominus$$

c. An ionization of the molecule or atom by impact and the adherence of the electron.

[5] Ozone, D. Van Nostrand, p. 107.

The electron, having in its course of flight lost much of its initial kinetic energy, may not, on contact with a neutral atom or molecule, possess sufficient energy to detach a valency electron, and may, therefore, actually adhere to the system it strikes, forming a negatively charged atom or molecule:

$$O_2 + \ominus = O^-_2$$
$$O + \ominus = O^-$$

Oppositely charged atoms and molecules may then react to form ozone:

$$O^+_2 + O^- = O_3$$

From such a consideration, one must agree with Rideal that a higher number of pulsations should result in greater ionization and higher ozone yields. With no attempt to split hairs, one may again refer to Table III, and here we find the ozone yield increased beyond the theoretical increase for wattage, if wattage alone is considered the determining factor, with no other condition altered than the frequency. The basis of impact and bombardments as the ionization mechanism, and ionization as the ozone forming agent, is well supported in the behavior of oxygen, which yields three times more ozone than air for the same set of conditions. More molecules of the reacting gas are present, hence more must receive the impacts.

McEachron[6] has shown that much poorer yields of ozone are obtained at pressures below the atmosphere than at atmospheric pressure. A consideration of these facts led the writer to the belief that a combination of high frequencies and high pressures would serve to better the efficiency of ozonizers, since one would have at once more pulsations and more molecules.

Some preliminary work was conducted in our laboratory, with the view of putting high frequency and pressure to test. This work indicated that an increase in both concentration and yield could be hoped for. Further and more careful work was then conducted, and sufficient data collected to demonstrate beyond doubt the enormous benefit to be derived from the combinations. With this in hand, we made application for letters patent on the

[6] Bulletin No. 9, Experimental Station, Purdue University, Lafayette, Ind.

combination of high frequency and high pressure as a means of increasing ozonizer efficiencies, and rendering possible the economical production of high concentration ozone.

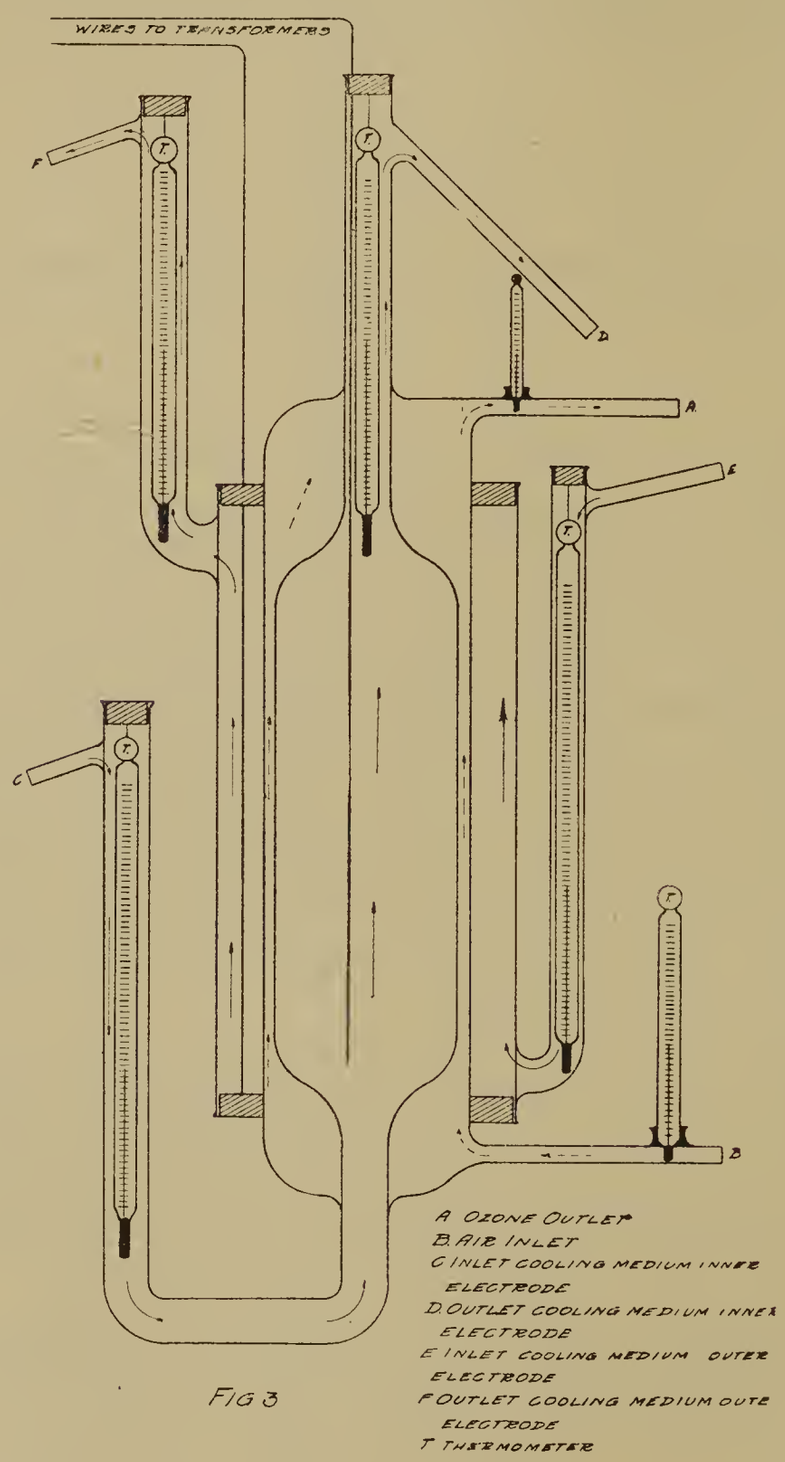

FIG 3

Table V sets forth some of the results obtained with the test ozonizer, using low frequency current (50 cycles). These tests were conducted to determine the effect of pressure apart from high frequency. It will be noted that one atmosphere pressure

makes it possible to obtain ozone concentrations in air which were hitherto obtainable only in oxygen. Three atmospheres pressure increased the yield per tube by 30 per cent over the best figures obtained at atmospheric pressure. Table VI sets forth some results obtained with higher pressures and higher frequency. From this, we can readily see the enormous advantage of this combination.

TABLE V.

Ozone Produced with Low Frequency Current.

Test No.	Frequency	Tension v.	Gas Flow L. P. M.	Gauge Pressure atm.	Concentration O_3 g./cu. m.	Yield per tube per hr.	Gas
42	50	25,000	0.71	1.0	46.3	1.92	Air
105	50	27,500	20.80	0.0	2.97	3.82	Air
121	50	27,500	26.8	3.0	3.15	5.02	Air

TABLE VI.

Ozone Produced with High Frequency Current.

Frequency	Tension v.	Gas Flow L. P. M.	Gauge Pressure atm.	Concentration O_3 g./cu. m.	Yield per tube per hr.	Gas
10,000	30,000	25	3.5	36.0	54.0	Air
10,000	28,000	25	3.0	31.0	46.5	Air
10,000	33,000	25	4.2	40.8	61.2	Air

In my opinion, the ionization theory, as outlined by Rideal, is the only one advanced so far which is tenable in the light of present knowledge. It is essentially an energy transmutation, and like all energy transmutations which are artificially effected, cannot attain to an efficiency of 100 per cent. Fig. 3 illustrates the apparatus used by Starke in the determination of the energy yield of ozone. The figure is self-explanatory, and Dr. Starke's results checked against careful measurements made electrically. This draws a clear cleavage for the utilization of the energy furnished an ozonizer.

Our problem is one of increased efficiency. High frequency has succeeded in increasing the yield per tube by simply increas-

ing the energy density. It has not increased the efficiency more than a negligible amount. Higher pulsations undoubtedly tend to increase the efficiency, but with the increased energy incidental to increased frequency, we suffer a thermal decomposition of ozone.

The heat conductivity of a gas is proportionate to its pressure, hence at higher pressures we are able to better conduct away the heat. This prevents, to some extent, the thermal decomposition of ozone, and is one of the advantages of its use, since it permits a slower gas velocity for a higher energy density with an accompanying increase in concentration. The higher the pressure of the gas, the greater number of molecules present, and hence the greater the chance of bombardment and accompanying ionization. So much may be said for pressure.

Now, with pressures and frequencies both elevated, we derive the joint benefits of two factors that both tend to increase yields per tube and efficiencies.

The net results of our work to date are briefly:

1. An increase in yield per tube by the use of high frequencies. This greatly cheapens the cost of large ozone producing plants.

2. The production of high concentration ozone on a commercial scale by the use of high pressures.

3. The opening up of an avenue of investigation that promises to lead to the increase of efficiency of commercial ozonizers.

In closing, it may be well to say that we have observed a further benefit in the use of higher pressures, since at pressures above 1 atm., the formation of the oxides of nitrogen seems to be entirely inhibited. Our work so far certainly presents entertaining possibilities and an incentive to pursue them to an issue.

DISCUSSION.

F. O. Anderegg[1]: Pressure reduces the mean free path of electrons, and therefore reduces the probability of collision with sufficient energy to activate nitrogen. Accordingly, you would

[1] Purdue University, Lafayette, Ind.

expect to get a decrease in the amount of nitrogen oxidized, but you would not secure complete elimination of oxides of nitrogen by simply doubling the pressure.

Mr. McEachron has carried out some work at varying pressures and at varying frequencies on both ozone and oxide of nitrogen formation.

K. B. McEachron[2]: The work with varying frequencies has only covered a narrow range. We worked from 30 cycles up to 120 cycles. Inside that range the maximum results were obtained at the lower frequencies. A study of our results at 30 cycles will show that the yield-flow curves have abrupt peaks. At 60 cycles, although the maximum yield was less than at 30 cycles, the curves are much smoother and the difficulties of control are not so great.

Concerning the effect of pressure, we found up to the atmosphere and a little above (750 mm.) that the yields of ozone and nitric oxides both increased with increasing pressure. How far that range can be extended I do not know. Perhaps the curve drops off a little above the atmosphere. I should say that something of that kind probably takes place, at least with nitric oxides.

It is of course extremely important for an ozone process that the oxides of nitrogen be excluded. In this connection I would like to ask Mr. Hartman how he measured his energy input.

Frank E. Hartman: The energy input was measured by a watt meter in the secondary circuit. Stark's energy measurements were made calorimetrically. We have made energy measurements by both methods and find the results in close agreement.

Fig. 3, page 236 of this paper, illustrates Stark's method of calorimetric measurement. The figure is self-explanatory. It may be added, however, that thermometers are so located as to indicate the temperature of the ingoing and outcoming gas. The ozone tube is so constructed that its glass parts serve only as dielectrics. The electrodes, consisting of dilute acid solutions are allowed to flow through the spaces provided, and thus serve as cooling media also. The acid solution forming the anode is insulated from that forming the cathode.

Thermometers are located so as to indicate the temperatures of

[2] Lightning Arrester Eng. Dept., General Elec. Co., Pittsfield, Mass.

the ingoing and outcoming acid solution. The total amount of acid solution used in a definite period of time is carefully weighed, and from its temperature increase the energy is calculated to watts. The same is done with the gas; the quantity of ozone formed is determined by analysis and its energy, on the basis of 34,000 cal. as the heat of formation, is calculated to watts. The sum of these calculations then represents the energy absorbed by the tube. In determining the efficiency of ozonizers, it is essential that the true watts be observed, since on increasing the current density the phase shifting is less pronounced, thus the power factor varies inversely as the current.

In an effort to reveal the effects of ozonizing at elevated gas pressures, one must never lose sight of the fact that the dielectric properties of a gas increase as the pressure. The literature records several adverse results with the use of elevated pressure simply because the potential was not elevated proportionately. If one elevates the gas pressure only the current falls, hence the tube is supplied with less energy. If one then elevates the potential to a value that gives a current flow equal to that obtained at atmospheric pressure, the efficiency of the ozonizer is increased. Raising the potential is productive of an increase in the total energy, above that used at atmospheric pressure, since the potential is elevated and the current remains the same. As I apprehend it, the presence of more molecules in the field of discharge, due to elevated gas pressure, produces an ozonizing condition of so much greater efficiency that the actual energy efficiency of the tube is increased. We have observed this increase in efficiency, to the extent of 30 per cent, by careful measurements.

F. O. Anderegg: We have here two different investigators, and there is no question about the reliability of the results. They simply used different tubes, under different conditions. I do not doubt that if Mr. Hartman and his friend had worked with their tube for a long time, and then had tried to repeat their first experiment, they would have gotten different results. That is due to surface changes which are apt to be extremely serious. These surface complications play "hob" with trying to draw real conclusions that mean anything with the silent discharge.

S. C. LIND[3]: We could not have a better illustration of a commercial electrochemical gas reaction than that of ozone formation. The final conclusion that an ionized oxygen molecule reacts with an ionized atom to form one molecule of ozone would lead to the ratio M/N = 0.5, which is in quite good accord with the best experimental data now existant. On the other hand, a theory of complex formation and accompanying participation by free electrons would lead one to expect a higher M/N ratio. This can be settled only by further experimentation.

FRANK E. HARTMAN: I have spoken of obtaining 100 per cent yields. Let me explain that we have not obtained 100 per cent efficiency of the power input, simply 100 per cent increase of current and ozone yield, with increasing cycles, as calculated from the formula on page 229. Ozone tubes are frequently erratic in their action.

Fries has patented the idea of recovering the spent ozone from ozonizing reactions and passing it again through the ozonizer. We have found that when ozone is present in the oxygen or air entering an ozonizer, the efficiency is decreased. We first noticed this when ozonizing oxygen taken directly from an electrolytic cell. Subsequent experiments with electrolytic oxygen, using chemically pure sulfuric acid diluted with conductivity water, revealed that as long as a reaction of an oxidizing agent was obtainable in the oxygen being used, the efficiency was bad. If the oxygen was allowed to stand, however, until a negative test was obtainable, or if it was passed through a hot tube of sufficient temperature to destroy any ozone present, normal results were obtained.

All ozonizers appear to decrease in yield after they have been in operation for a while. In an effort to apply ozone quantitatively one should provide at least 25 per cent over capacity, based on the output of the ozonizers when new. Our practice is to rate an ozonizer that produces 20 g. of ozone an hour when new, at 15 g. On several years operation, we have found that they will not decrease below this amount.

K. B. MCEACHRON: Mr. Hartman has stated that an increase in energy density means increase in yield. This may be based,

[3] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.

as he has done, on increase of current or it may be based on increase of voltage. The first is obtained in this case by increasing the frequency, the second may be obtained by decreasing the frequency.

Although the best results were obtained with increased frequency and increased current, it seems to me desirable to investigate also the other side of the question wherein the voltage is increased. I do not believe that sufficient data are at hand to state definitely that this reaction is a function of the current and the resistance without considering the voltage.

S. C. Lind: It seems clear that ions are not the answer to activated nitrogen either in its reaction with nitrogen or hydrogen, because in the case of α-particle bombardment, where we know we have the ions, we do not get combination of nitrogen with oxygen and we do not get ammonia formation in the case of hydrogen. Therefore, if the activation of nitrogen is not of the ionic form, it must be of the form discussed by Compton; that is, intra-atomic activation, or what is usually called resonance. That being the case, it looks as if we might get our oxides of nitrogen through resonance and our ozone through ionization. If we know under what conditions we get the one or the other, we might be able to predict when we will get ozone and when oxides of nitrogen.

F. A. Lidbury[4]: What is the cost of an apparatus to produce 1 kilogram of ozone per hour?

Frank E. Hartman: The cost up to date has not been reduced for the reason that no industrial plant, using high frequency, has been placed in operation. It is necessary to install a fairly large plant in order to derive any benefit from the use of high frequency, as the cost of high frequency alternators must be absorbed. I think the smallest high frequency plant that will be economically feasible will be in the neighborhood of 50 Kw. For capacities lower than this it is advisable to utilize the frequencies available from commercial circuits.

The inductor type of high frequency alternator should be built cheaper than low frequency machines. But the use at present is

[4] Works Manager, Oldbury Electrochemical Co., Niagara Falls, N. Y.

so sparing, they are considered as special by manufacturers of electrical machinery, and in consequence carry in the price all that the word implies.

C. P. MADSEN[5]: I would like to ask Mr. Hartman whether he has tried other well known methods of generating high frequency currents at high voltages, other than the Alexanderson machine. For instance, there are tubes and the quenched spark gap with condensers, such as are used by Dr. Northrup.

FRANK E. HARTMAN: We have found that the manufacturers' guarantee, as regards the life of tubes, is not sufficient to make them of practical value for the present, but we believe that the future development will be in the direction of tubes. We have not investigated the use of the quenched spark gap for ozonizing, but are of the belief that its efficiency is too low.

[5] Consulting Engineer, New York City.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

HEAT LOSSES AND CHEMICAL ACTION IN THE HIGH VOLTAGE, HIGH FREQUENCY DISCHARGE THROUGH AIR.[1]

By Farrington Daniels,[2] Paul Keene,[3] and P. D. V. Manning[4].

Abstract.

A discharge was produced by a Tesla coil at about 100,000 volts, in a large chamber constructed from a terra-cotta sewer pipe. A central wire 91.5 cm. (36 in.) long and a wire screen 41 cm. (16 in.) in diameter formed the electrodes. Outside of the netting was a large cylinder of paraffined paper, and the whole chamber was arranged to function as a calorimeter. Of the electrical energy supplied to the primary of the transformer 40 to 50 per cent appeared as heat in the discharge chamber and 1 to 2 per cent as chemical energy. The air was analyzed for ozone and nitric acid. There is no advantage in discharges of this type for fixing nitrogen. The "cold" discharges waste just as much electrical energy in the form of heat, as do the arcs, the only difference being that the consumption of electrical energy is small and so the temperature rise is less.

The chemical action of all electrical discharges in air consists of two fundamental reactions—the formation of ozone, and the formation of nitric oxide. Both are endothermic compounds which exist at room temperature in an unstable condition, and tend to decompose with increasing rapidity at higher temperatures. The two reactions differ, however, in that ozone decomposes instantly above 200° C., while nitric oxide does not suffer immediate decomposition until a temperature of 1200° C. is attained.

[1] Manuscript received June 26, 1923. Contribution from the U. S. Bureau of Soils and the U. S. Fixed Nitrogen Research Laboratory.

[2] Laboratory of Physical Chemistry, University of Wisconsin, Madison, Wis.

[3] The Solvay Process Co., Syracuse, N. Y.

[4] Bregeat Corp., New York, N. Y.

At still higher temperatures small quantities of the substances are formed according to the thermal equilibrium. In removing them from the region of high temperature they are more or less completely decomposed, depending on the speed of their passage through the adjacent regions which are cooler, but still above these "freezing temperatures" at which they can exist for appreciable lengths of time.

In addition to these two fundamental reactions, several secondary reactions may occur. At temperatures below 500° C. the nitric oxide unites with oxygen to form NO_2, and below 120° the NO_2 polymerizes to N_2O_4, and NO_2 and NO unite to form N_2O_3. At temperatures not too far above room temperature ozone oxidizes the other oxides of nitrogen to nitrogen pentoxide, and nitrogen pentoxide unites with moisture in the air to form nitric acid. These temperatures are not sharply defined because the equilibria change gradually with the temperature.

The extent of these secondary reactions depends on the nature of the discharge. In a flaming arc the "temperature" is very high, and nitric oxide is formed, which on cooling forms NO_2 and N_2O_4 with the oxygen of the air. No ozone results because that which is formed is completely decomposed in passing through the outer regions of the arc. In a spark discharge also nitric oxide is produced, but the temperature of the shell of gas surrounding the spark is still high enough to decompose the ozone before it can get out. In the "brush discharge" both nitric oxide and ozone are formed, and by their combination nitrogen pentoxide is produced. The uniform or so called "silent electric discharge" is a comparatively cold discharge. This is the least favorable type of discharge for nitric oxide formation, because the kinetic energy corresponding to temperature is low, but on the other hand it is the most favorable type for ozone formation because the decomposing action in the gas surrounding the microscopic streamers of the discharge is slight.

There are various gradations between the silent or smooth discharge, the brush, and the spark, which affect the chemical products to a considerable extent. The more discontinuous the discharge and the greater the intensity of the streamers, the

greater is the proportion of nitrogen pentoxide. If sparking becomes frequent all the ozone is decomposed and then nitrogen peroxide instead of the pentoxide is formed.

It is essential to register a strong reservation in regard to the use of the word "temperature" as applied to an electrical discharge. Ames[5] among others has pointed out that one cannot speak properly of the temperature of a mass of disturbed molecules of this kind. In an electrical discharge certain molecules acquire an electrical charge and are moved with high velocity in the electrostatic field. Free electrons are moved with still greater velocities. Other molecules in the path are ionized by collision and are given accelerated velocities by the field, so that regions of high kinetic energy result. This high velocity of the molecules and ions is equivalent to a high temperature, but the distribution of velocities does not follow Maxwell's distribution law. It is not possible then to ascribe a definite temperature to the discharge, or even to smaller regions within it, and much less to a single molecule or ion.

The classical controversy as to whether the formation of nitric oxide in the arc is a purely thermal process or an electrical phenomenon becomes then superfluous. Qualitatively, it is proper to consider an arc as a region of high temperature, but thermodynamical calculations based on a definite temperature of an arc or an electrical discharge are unsound. The gas immediately surrounding such a region does have a "real" temperature, and this temperature determines the themodynamic equilibrium of the gases which leave the arc. It is evident that the concentration of endothermic compounds in the electrical field, may be much greater but it cannot be calculated quantitatively because a definite temperature cannot be ascribed to it. Furthermore, it is of little practical importance any way, for the products cannot be removed without going through this region of lower kinetic energy, where a real equilibrium with a lower concentration of the endothermic compounds is established. For calculations of equilibrium then the temperature should be that of the region immediately surrounding the electrical discharge, but outside of the electrical field. One can say then that an electrical equili-

[5] Ames, Bull. Am. Inst. Min. and Met. Eng. 2482 (1919).

brium exists which gives a higher concentration of the products (NO and O_3) than the thermal equilibrium.[6]

According to thermal calculations which have been based on an assumed temperature of the arc the yields of nitric oxide in the arc process are limited to small quantities, because 97 to 98 per cent of the energy is consumed in heating up the excess of un-

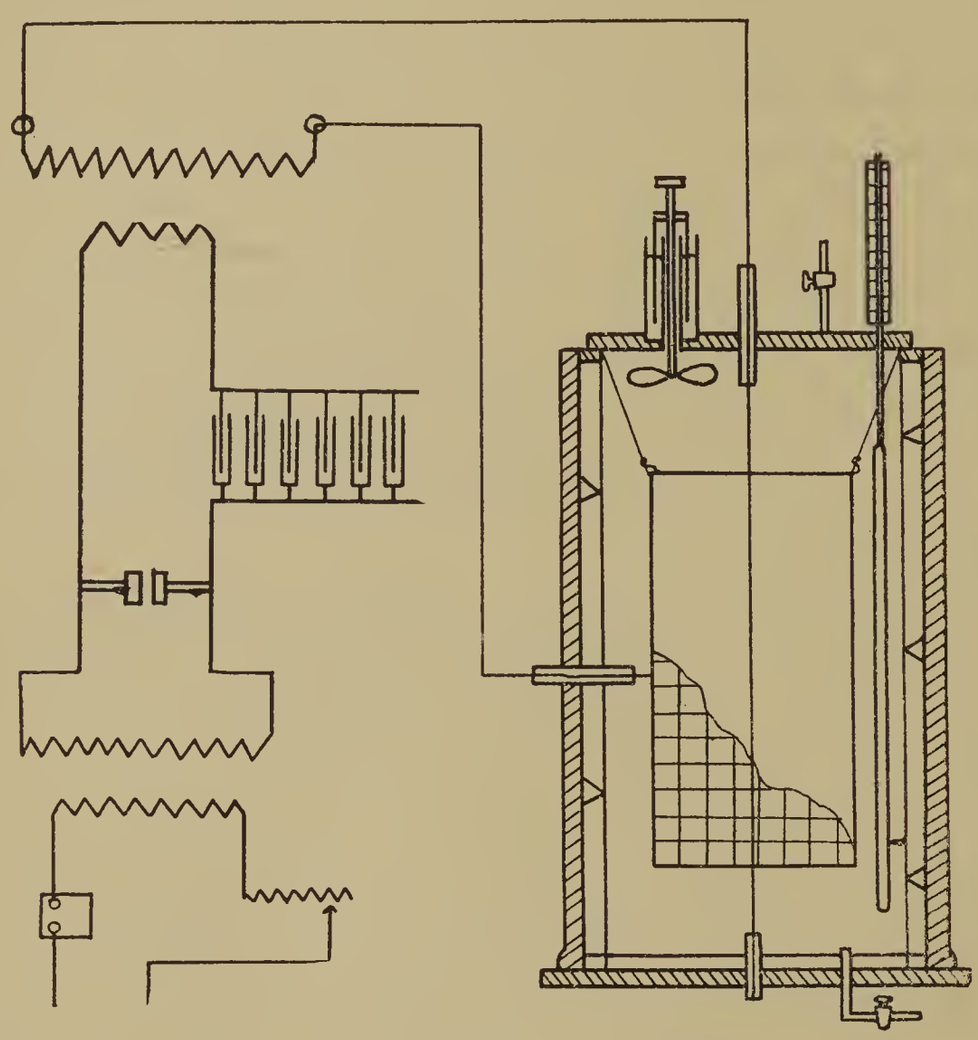

FIG. 1
Apparatus for measuring the heat evolved and the chemical products formed in the high voltage, high frequency discharge.

changed air to high temperatures.[7] It has been thought by some that the corona or silent discharge and the brush discharge would not waste this energy as heat, because they are cold discharges as compared with the hot spark discharge or the still hotter arc. Some enthusiasts have gone so far as to believe that the theoretical limit lies in the thermo-chemical heat of formation of the

[6] Holwech and Koenig, Z. Elektrochem. 16, 803 (1910).

[7] Haber, "Thermodynamics of Technical Gas Reactions" (Translated by Lamb), 268, Longmans Green & Co. (1908).

products. The results of this investigation show, however, that the relation between electrical consumption, heat evolution and chemical action, is of the same order of magnitude in the corona as in the arc. The corona appears "cold," because the consumption of electrical energy per volume of gas is small.

The high-voltage, high frequency corona more nearly approaches the nature of many little sparks. It differs considerably from a direct current or low frequency corona in being less uniform. It consists largely of long streamers which are like small sparks, except that they do not reach across the whole distance between the electrodes. This type of corona appeared to be well worth investigation, particularly as regards the formation of nitrogen pentoxide and nitric acid. A corona was produced in air around a wire, by an oscillation transformer of the Tesla type at approximately 100,000 v. and 200,000 cycles. Since accurate electrical measurements of such a circuit are difficult, the energy used up in the corona discharge was determined by calorimetric means. The chemical changes taking place in the corona were determined by sweeping out the air, and titrating for ozone and nitric acid. The experiments showed that the fraction of electrical energy which could be converted into chemical energy was no larger than has been reported for various other types of discharges and arcs, but that the ratio of nitric oxide to ozone was somewhat higher than that reported in other discharges.

The electrical circuit[8] and discharge chamber are shown in Fig. 1.

Current at 110 v. and 60 cycles passed through the watt meter, the variable inductance, and the primary of the 1 kw. transformer. The secondary of the transformer stepped the voltage up to 15,000 and charged the condenser, until it broke down across the rotary spark gap. The capacity of the condenser could be varied from 0.002 to 0.024 microfarad. In surging back and forth across the spark gap to give a series of oscillatory discharges, the current passed through the primary of an oil-immersed Tesla coil. The voltage of its secondary was varied roughly by changing the distance of the spark gap and a maximum of about 100,000 v. was obtainable. The current consisted of quickly damped oscilla-

[8] The electrical equipment was furnished by the American Transformer Co., Newark, N. J.

tions separated by comparatively long period of time in which no current flowed.

A large terra-cotta sewer pipe 91.5 cm. (3 ft.) high and 51 cm. (20 in.) in diameter, served as the outer wall of the discharge chamber. Inside of it was attached a slightly smaller cylinder of paraffined paper supported by corks. The bottom was tightly closed with a sheet of impregnated fiber over which a thick layer of paraffin was poured, making an effective seal. A fiber ring over which melted paraffin was poured closed the opening at the top between the paper cylinder and the terra-cotta pipe. A fiber top was laid on this ring and rendered gas tight with paraffin. The central wire, of No. 22 copper, was held tightly by fiber bushings embedded in paraffin. The outer electrode consisted of a 41 cm. (16 in.) cylinder of galvanized fence netting with meshes 1.3 cm. (½-in.) square. Such netting behaved as a plate toward the high voltages, and yet permitted free circulation of air. It was suspended in place by four pieces of asbestos cord. Connection with the transformer was made through a glass tube filled with paraffin protruding through a hole in the side. The central wire and netting were protected from chemical action by paraffin.

Ample stirring was effected by a paper pin-wheel fan connected to a fiber rod and rotated at a high speed by a belt from a small motor. The axle rotated in a glass bearing and a deep mercury seal served to keep the chamber gas tight. A small glass window in the cover made possible the visual observation of the discharge.

A tall oil manometer set into the cover gave a direct reading of the gas pressure. The rise in temperature was measured by a Beckman thermometer and by a large toluol thermometer, the bulb of which extended the full length of the chamber between the outer electrode and the paper cylinder. In this way it was kept out of the discharge field, but still within the well stirred air chamber. It was calibrated against a Beckman thermometer in a tall water bath.

The thermometers were placed outside of the electrical field to avoid heating by induction. The toluol thermometer was used because the space above the mercury of the Beckman thermometer became luminous if placed near the electrodes. As a rule, however, the Beckman checked with the toluol thermometer.

The heat absorbed corresponding to the temperature rise in an experiment was determined, with the aid of a calibrated voltmeter and ammeter, by passing an electric current from a storage battery through a long resistance wire placed at the center of the chamber. Errors due to heat losses were minimized by making a number of calibrations with different rates of heating. The apparent heat capacity for any individual experiment was then found by interpolation on a curve.

Immediately after an experiment the gases were swept out into the absorbing system, with dry CO_2-free air. The first bottle and chain of bulbs contained a measured quantity of sodium hydroxide and a second, similar unit was filled with neutral potassium iodide solution. All connections were made with glass tubes and overlapping joints sealed with paraffin. Back-titration of the alkali with standard acid gave the number of grams of nitric acid produced. The ozone was determined by titration of the potassium iodide solution with 1/10 *N* sodium thiosulfate after acidifying. The oxidized nitrogen was always in the form of N_2O_5 when free ozone was present.

In carrying out an experiment the chamber was filled with pure, dry air and tested for leaks. The fan was started and readings of the special toluol thermometer were taken every minute. The current was turned on for a definite period of time, usually three minutes, and temperature readings were recorded every quarter or half minute. The adjustments of the electrical circuit were made before starting the experiment. Frequent observations of the discharge were taken through the window in the cover. The appearance of the discharge changed with time and as it continued the bluish, uniform glow became less intense and finally disappeared, while the pinkish streamers became more pronounced. If the discharge filled the whole chamber at the start, it usually gave rise to frequent sparking, if continued for a longer time than three minutes.

The data of a typical experiment (No. 77) will serve to illustrate the calculations involved. Six Leyden jars with a total capacity of 0.012 microfarad were used and the spark gap was set at 0.24 cm. (0.09 in.) a distance which under the conditions was found to give as bright a brush discharge as possible, without

sparking. The circuit was closed for a period of 3 min. No sparking occurred in the chamber. The maximum rise of the toluol thermometer was 156.6 mm., corresponding to 3.46° C. By interpolation on the calibration curve it was found that a maximum rise of 3.46° C. with 3 min. heating was accomplished by the addition of 13,650 joules.

The watt meter in the primary circuit registered between 165 and 170 with an average of 168 w. The electrical energy used up by the whole system was then 3 x 60 sec. x 168 w. = 30,300 joules. The fraction of the total electrical energy which appeared as heat in the discharge chamber was 13,650/30,300 or 45 per cent. Losses in the transformers, spark gap, condensers, and lead wires made up most of the other 55 per cent.

Titrations of all the absorbing units showed that 0.0109 g. of nitric acid and 0.113 g. of ozone had been produced. These weights multiplied by 20 gave 0.218 and 2.26 as the yield per hour. Multiplying again by 1000/168 gave 1.3 g. of nitric acid and 13.4 g. of ozone per kw.-hr. The ratio of ozone to nitric acid was then 10.3 by weight.

One mole of N_2O_5 was made by the reaction of two moles of NO, or NO_2 and one mole of O_3[9]. One mole of N_2O_5 gave two moles of nitric acid (126 g.) with the water of the absorbing system. The two moles of NO absorbed 42,000 cal., while 34,000 cal. were required to produce the one mole of ozone, according to thermo-chemical data. 2520 joules (=(42,000 + 34,000) x 4.18 /126) were absorbed in the formation of endothermic compounds, which reacted to give 1 g. of nitric acid. It is believed that this value should be used rather than the value based purely on the heat of formation of nitrogen pentoxide,[10] for it takes into consideration the actual steps in the reaction. Furthermore, 2,960 joules (=(34,000 x 4.18/48) were required to produce 1 g. of ozone. Adding the energy absorbed in producing the nitric acid and ozone in Experiment No. 77 gave 363 joules (0.0109 x

[9] Wulf, Daniels and Karrer, J. Am. Soc., 44, 240 (1922).

[10] See for example Harding and McEachron J. Am. Inst. Elec. Eng. page 413, 1920, where the value of 399 joules per gram of nitric acid is calculated. To make this point clearer, if the gases were passed through a cold tube *solid* N_2O_5 would be formed. The heat of formation of solid N_2O_5 is exothermic whereas that of gaseous N_2O_5 is endothermic. If one took the heat of formation of the solid N_2O_5 for calculation, no energy would have to be supplied by the discharge. As a matter of fact the gaseous N_2O_5 must be formed first with the absorption of energy from the discharge, and the heat evolved in the second step *i. e.*, the condensation to a solid cannot be used in the first step.

2520 = 28 + 0.113 x 2960 = 335). The fraction of the total electrical energy which was used in producing chemical action was then 1.2 per cent (363/30,300).

A large number of experiments were performed in order to study the influence of the various factors affecting the chemical action of the discharge. Since space is limited only the last ten are given in Table I.

TABLE I.

Effect of Various Factors on the Chemical Action of Electrical Discharges in Air.

Exp. No.	Time Sec.	Watts Prim.	Electrical Input Joules	Heat Discharge Joules	Heat / Prim. Input Per Cent	HNO_3 per Kw-hr.	O_3 per Kw-hr.	O_3 / HNO_3	Chem. Energy / Prim. Input Per Cent
75	36	80	2,880	1,860	64.6	3.57	18.35	5.2	1.73(*a*)
76	900	78	70,200	34,220	48.8	2.94	7.11	2.4	0.79(*b*)
77	180	168	30,300	13,650	45.0	1.30	13.4	10.3	1.20(*c*)
78	180	168	30,300	12,520	41.4	1.34	12.5	10.9	1.08(*c*)
79	180	168	30,300	13,450	44.4	0.40	3.07	7.8	0.28(*d*)
80	180	168	30,300	13,450	44.4	1.66	5.52	3.3	0.57(*e*)
81	180	162	29,150	13,010	44.7	0.98	11.10	11.0	0.92(*f*)
82	180	168	30,300	11,590	38.3	0.64	7.28	11.4	0.64(*g*)
83	180	63	11,340	3,850	33.9	0.73	9.62	13.1	0.85(*h*)
84	180	64	11,500	4,902	42.6	0.65	10.8	16.0	0.93(*h*)

(*a*) Short Exposure. (*b*) Long Exposure. (*c*) Check Experiment. (*d*) Decomposition Standing. (*e*) Excess Oxygen Sparking. (*f*) Reduced Pressure. (*g*) Excess Moisture. (*h*) Smaller electrode distance.

Experiments No. 75 and No. 76 show the influence of the duration of the discharge on the yield. It is evident that better yields were obtained for short periods than for long. This fact agrees with many observations in the literature that in continuous gas flow experiments with electrical discharges a low concentration of products is associated with a high yield in g. per kw.-hr.[11, 12, 13]. In No. 76 violent sparking occurred after the first 5 min.

Experiments No. 77 and No. 78 give an idea of the reproducibility of results, when conditions are kept as nearly identical as possible.

[11] Rideal "Ozone," page 109, D. Van Nostrand (1920).

[12] Anderegg, Proc. Indiana Acad. Sci. 163, (1921).

[13] McEachron and George, Bulletin No. 9, Experiment Station, Purdue University, page 161.

In No. 79 the products of the discharge were left in the chamber over night, before sweeping out. It is evident from the low yields that the gases should be analyzed soon after an experiment.

A large excess of oxygen changed the type of discharge, caused considerable sparking, and resulted in a low chemical yield as shown in No. 80.

At 650 mm. pressure, in No. 81, the spark gap was shortened to avoid sparking in the discharge chamber, but the results were about the same as in experiments at atmospheric pressure.

When the air subjected to the discharge was saturated with water vapor, a lower yield results as shown in No. 82.

In No. 83 and No. 84 a smaller cylinder of iron netting was used so that the distance between electrodes was 10.2 cm. (4 in.) instead of 20.4 cm. (8 in.) as in the previous experiments.

The electrical variables, such as frequency, were not studied. It is believed that they do not have any influence on the chemical products under these conditions except insofar as they change the character of the discharge. In some of the experiments, not recorded here, the areas of the two electrodes were equalized by connecting two identical chambers in parallel, so that each terminal of the Tesla coil was connected to the netting of one chamber and the central wire of the other. The sum of the heat effects and the chemical reactions in the two were practically the same as those obtained with a single chamber. In fact nearly all of the earlier experiments gave results which fell within the range of the ones presented here.

CONCLUSIONS.

1. Short exposures to the electrical discharge gave a higher chemical efficiency than long ones.

2. The ratio of ozone to nitric acid varied from 16 to 2.4. This ratio depended chiefly on the character of the discharge. The more intense the pink streamers the more nitric acid was produced. The more uniform the blue corona the greater was the proportion of ozone.

3. Sparking destroyed ozone and did not greatly increase the yield of nitric acid.

4. Approximately 45 per cent of the total energy supplied to an oscillation circuit of the Tesla type was evolved as heat in a large discharge chamber containing air.

5. Approximately 1 per cent of the total energy was used in chemical action. Of the energy actually supplied to the discharge chamber about 2 per cent was converted into chemical energy and 98 per cent into heat. This chemical efficiency is of the same order of magnitude as obtained in arcs and in other types of corona discharges in air. The so-called "cold discharges" waste as large a fraction of their energy in heat as do the arcs. It is significant that in spite of the large number of experiments by different investigators on the passage of electricity through air in various types of apparatus and under radically different conditions the maximum chemical efficiency remains limited to a few per cent.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Duncan MacRae in the Chair.

THE FORMATION OF GASEOUS IONS IN THE OXIDATION OF NITRIC OXIDE.[1]

By A. K. Brewer[2] and Farrington Daniels.[2]

Abstract.

Experiments with a special form of chamber show that when nitric oxide is oxidized between oppositely charged electrodes a current of electricity passes through the gases. The current is of the order of 10^{-14} amp. for the oxidation of 50 cc. of nitric oxide per minute reacting in a field of 450 v. per cm. This corresponds to about one ion for every 10^{13} molecules reacting. The current is directly proportional to the voltage and to the number of molecules reacting. No evidence of a saturation current could be detected. The precautions necessary to exclude extraneous charges and obtain reproducible results are given. Various hypotheses are advanced to explain the results.

The hypothesis which pictures the atom as a positive nucleus surrounded by negative electrons has been so well established by experiments, and has led to such far reaching advances in chemistry and physics, that it may be accepted without reservation. In a chemical reaction when atoms change from one molecule to another, one might expect some of the electrons to be loosened and to give rise to electrical charges. The experiments described here show that ions can be formed when nitric oxide is oxidized in an electrical field.

It has been recognized for a long time that an important relation probably exists between chemical action and ionization, but the exact nature of the relation has not been clear. The important

[1] Manuscript received June 26, 1923. Contribution from the Laboratory of Physical Chemistry, University of Wisconsin, Madison, Wis.

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work of Lind[3] has shown that in many reactions induced by alpha particles, it is approximately true that the number of ions formed and the number of molecules reacting is the same. Whether ionization is the cause of chemical reaction, or the result, or whether both are independent results of the same process has not yet been decided definitely.

It is known that a strong electrical discharge will produce both chemical action and ionization, and it becomes of great importance to know whether chemical reaction will produce ionization when the electric field is insufficient to produce it. This question has been studied by a number of investigators[4] but the conclusions are inconsistent and unsatisfactory.

It has been shown by Haber that ionization frequently results from a change in phase, as for example in the bubbling of a gas through water. In general Haber found no ions unless there was a change in phase. Reactions completely in the gas phase offer the best opportunity for study, but it becomes particularly necessary to guard against the formation of a liquid or solid phase. Pinkus[5] reported ionization in certain gas reactions but his results were not always consistent. He concluded that the oxidation of nitric oxide does not give ions, but his apparatus was smaller and less sensitive than the one described here.

In the present paper experiments on the ionization accompanying the oxidation of nitric oxide are described. This reaction is particularly suitable for study because it is a comparatively slow reaction, and therefore distributes any ionization effects over a large area of electrode surface. In a very rapid reaction, any ionization would be concentrated at the entrance of the chamber, and the large electrodes would be no more effective in detecting minute ionization currents than small electrodes. It has the further advantage that the rate of reaction is nearly independent of temperature. It is complicated, however, by the reactions, $2NO_2 \leftrightarrows N_2O_4$ and $NO + NO_2 \leftrightarrows N_2O_3$, which occur simultaneously with the slower reaction $2NO + O_2 \leftrightarrows 2NO_2$. Further-

[3] Lind, Chemical Effects of Alpha Particles, 115, Chemical Catalogue Co., (1921).

[4] L. Bloch, Comp. rend. **150**, 694; De Broglie and Brizard, Comp. rend. **150**, 969, Radium **7**, 164; Haber and Just, Z. Elektrochem. **20**, 783 (1914); Reboul, Comp. rend. **149**, 110; Trautz and Henglein, Z. anorg. Chem. **110**, 237-89 (1920).

[5] Pinkus, J. Chim. Phys. **16**, 201, **18**, 366, **18**, 412; Helvetica Chim. Acta **1**, 141, **4**, 288 (1921).

more the NO_2 and probably the N_2O_3 are colored, a fact which might indicate the presence of an electron in a less stable condition.[6] There is evidence, however, that this color does not imply the existence of an easily ionizable substance.[7]

DESCRIPTION OF APPARATUS.

The reaction chamber, shown in Fig. 1, consisted of two concentric, cylindrical electrodes, between which the gaseous reaction took place. The outer electrode was charged to any desired potential by a battery of dry cells, while the inner electrode was connected to the ground through an electrometer. The two electrodes were set on bakelite supports mounted on a grounded plate.

The outer electrode was a glass tube 10 cm. in length and 2.8 cm. in diameter, provided with a constricted neck. Two inlet tubes were so arranged that the two reacting gases were mixed within the electric field. The entire inner surface was covered with a heavy film of platinum, deposited by cathode sputtering. Electrical contact was made by means of a platinum wire twisted tightly around the platinized neck.

The inner electrode was a glass tube 16 cm. long and 8 mm. in diameter, coated for a distance of 11 cm. with platinum by the reduction of platinum chloride. Contact was made with a platinum wire leading out through the interior of the tube. A glass cup, connected to a suction pump, removed the gases which had passed through the chamber. A charge could be transmitted from the outer to the inner electrode only by passage through the gas between the electrodes.

The reaction chamber was enclosed in an insulated and grounded electric furnace so that it could be heated up to 100° C. or more.

The apparatus used for measuring the current across the gas space is shown in Fig. 1. The whole apparatus was set on a grounded metal table, and covered with a grounded cage, the wires were protected by insulators set on grounded metal plates, and special attention was paid to connections and to the small platinum switches. In fact all the precautions necessary for precision work of this character were observed.

[6] Langmuir, J. Am. Chem. Soc. **41**, 898 (1919).
[7] Burger and Koenigsberger, Physik Z. **13**, 1198.

A high resistance of the radio-active leak type was shunted across the electrometer. Pitchblende was cemented to an adjustable copper plate in an insulated copper box. An insulated copper plate was connected to a 22,000-ohm bridge with a fall of 4.5 v.

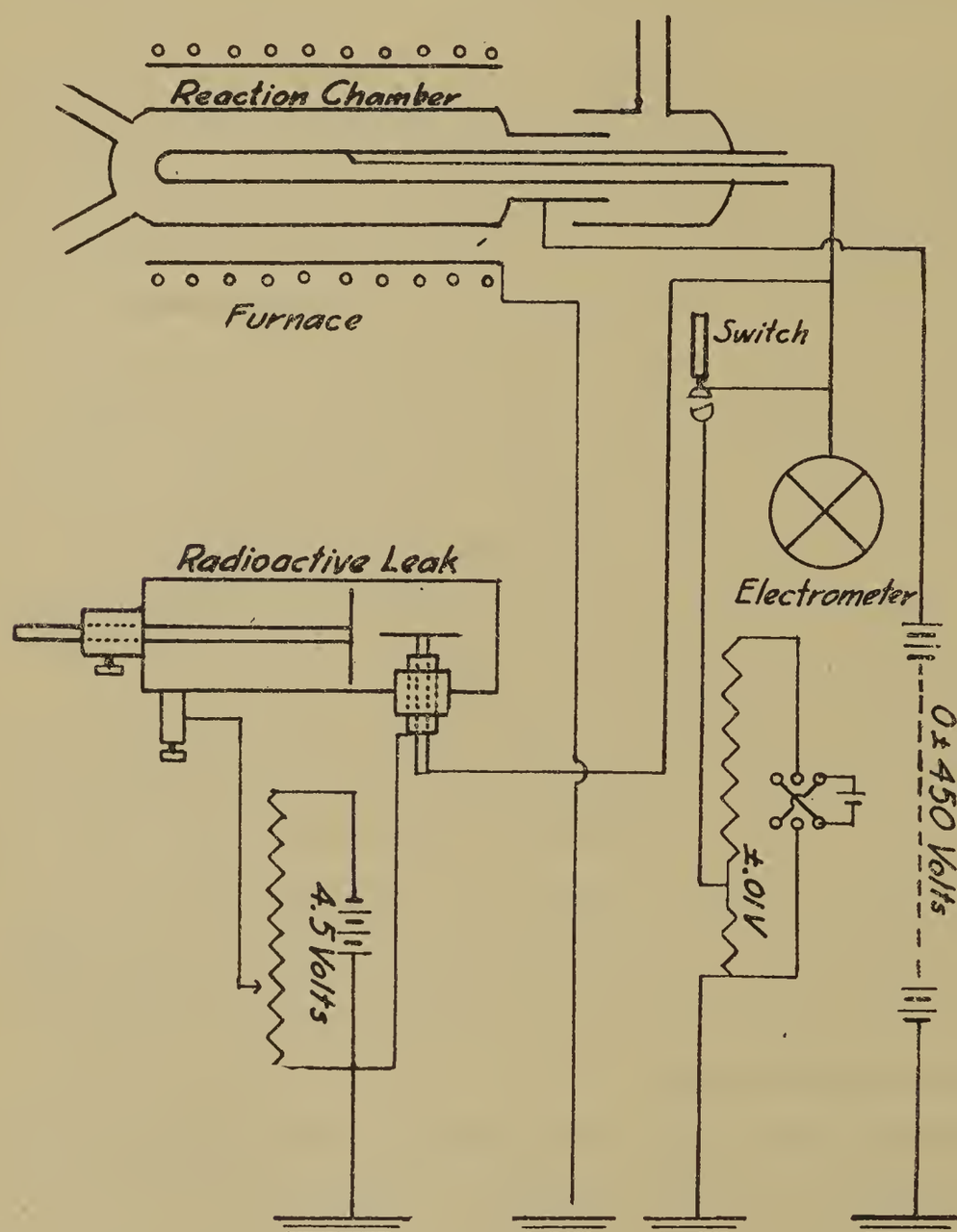

Fig. 1

across its terminals. The electrometer could then be used as a zero instrument, but it was found more convenient in practice to keep the adjustment of the radio-active leak constant during an experiment and read the deflections. The Compton quadrant electrometer was frequently tested for sensitivity with a standardized e.m.f. of 0.01 volt. A sensitivity of 7000 mm. per v. was

satisfactory. The capacitance of the whole system was determined by measuring the rate of discharge through the leak after charging to a definite voltage, and again after charging to the same voltage with the addition of standard capacitances to the system. From the rate of discharge and the capacitance of the system it was possible to calculate the resistance of the radio-active leak.

The potential to which the inner electrode was charged was calculated by the deflection of the electrometer and its known sensitivity. This voltage divided by the resistance of the radio-active leak gave by Ohm's law the current flowing from the outer to the inner electrode. In all the experiments the electrometer deflection was steady to at least 5 mm., corresponding under the conditions of the experiments to 7×10^{-15} amp.

PURIFICATION OF MATERIALS.

The nitric oxide was prepared by the action of dilute sulfuric acid on sodium nitrite. The gas was passed from the generator through a wash bottle filled with concentrated sulfuric acid and a P_2O_5 tube to a two liter reservoir containing concentrated sulfuric acid. It was stored here in order to remove ions which were generated by the bubbling and to absorb traces of NO_2. From the reservoir the nitric oxide passed through a flow meter with concentrated sulfuric acid in the manometer, thence through three large U tubes filled with glass wool and resublimed P_2O_5, into the reaction chamber.

Electrolytic oxygen from a tank was dried with sulfuric acid, and four large U tubes filled with resublimed P_2O_5 on glass wool. A flow meter, using concentrated sulfuric acid for the manometer liquid gave the quantity of oxygen passing.

Glass joints were used throughout the apparatus and syrupy phosphoric acid was used exclusively as a stop cock lubricant.

EXPERIMENTAL DETAILS.

In carrying out an experiment a large excess of oxygen (650 cc. per min.) was allowed to flow through the chamber constantly. The voltage applied was varied from + 453 to — 453 v. Since the distance between electrodes was 1 cm., the voltage impressed on the electrodes was also the potential gradient. The potential across the radio-active leak was adjusted to give a suitable zero

point, which remained constant indefinitely. When nitric oxide was admitted the electrometer was deflected and reached a constant reading as long as the flow of nitric oxide remained constant. After shutting off the nitric oxide and sweeping out the gases with oxygen, the electrometer returned to its original zero.

The facts that the results were reproducible, and that they fell consistently on straight lines, show that no accidental phenomena such as chemical action on the electrodes, condensation of liquids, frictional charges, or thermal effects were being measured. These factors can readily mask the small ionization effect, and are themselves exceedingly erratic. It seems not unlikely that the disagreement in the literature as to whether or not electrical charges are produced in gaseous reactions, has centered around these accidental phenomena. It is probable that the very small ionization currents can be measured with more certainty and greater accuracy in the apparatus described here than in the apparatus of the previous workers in this field.

The following experiments showed, it is believed, that these extraneous phenomena had been eliminated. Oxygen alone was passed through the chamber while the electrodes were charged. The oxygen was swept out with nitrogen and then pure nitric oxide was passed through. After again rinsing with nitrogen, air was passed through liquid N_2O_4 and then through the chamber. Then the gases were mixed as before but the electrodes were not connected to the battery. In none of these tests was there any movement of the electrometer, showing that the gases alone were not ionized and that chemical action of the gases on the electrodes was not the cause of the current. These tests were repeated many times, sometimes with rapid gas currents and the steadiness of the electrometer zero showed that frictional charges were not being produced.

Hot air was blown through the cold chamber. Again the chamber was slowly heated to above 100° C. in the electric furnace surrounding it. The fact that no movement of the electrometer could be detected showed that no thermo-electric effect was being measured. This test was considered necessary because the chamber became warm from the heat of the reaction when large quantities of nitric oxide were oxidized.

When the chamber was kept at about 100° C. no great difference was noticed in the deflections. This fact showed that the condensation of a liquid was not occurring, for even if water or nitric acid had been present they would have condensed to a much less extent at 100° than at room temperature.

It was only after two years of continuous effort that the disturbing influences were eliminated. A few of the precautions which were found necessary are given here. It was found necessary to dry the gases thoroughly, with sulfuric acid and P_2O_5. The gases could not come in contact with any organic matter. No rubber connections nor stop-cock grease were permissible. Lead glass for sealing in platinum wires was unsatisfactory, presumably because of chemical action. Ionization chambers in which there was a continuous surface of glass between the two electrodes could not be used.

The chamber had to be frequently dismantled, washed, dried and heated. Often the readings became erratic and the electrometer would fluctuate, going off the scale, sometimes in the wrong direction. Experience showed that it was then useless to continue the work further. However, after cleaning and heating the chamber the original results were reproduced. Possibly the difficulty was caused by a trace of moisture.

RESULTS.

The results are shown in Fig. 2, 3, and 4.

The points in Fig. 2 comprise the data of three check experiments extended over a period of two weeks. In these experiments the flow meter was not used but the flow of nitric oxide was kept the same, as determined by the levels of sulfuric acid in the reservoir. When the outer electrode of the chamber was connected to the negative terminal of the battery, a greater current was produced than when the positive terminal was connected. Since the central electrode (connected to the ground through the electrometer) had the opposite sign, it is clear that the negative ions had the greater mobility, a fact which is in accord with other observations in physics. When the outer electrode was negative the current was 9.7×10^{-16} amp. per v. per cm., and when it was positive the current was 8.3×10^{-16} amp.

In Fig. 3 the influence of different rates of flow of nitric oxide on the ionization current is shown. It is evident that the ionization current is directly proportional to the amount of chemical reaction at a constant potential gradient.

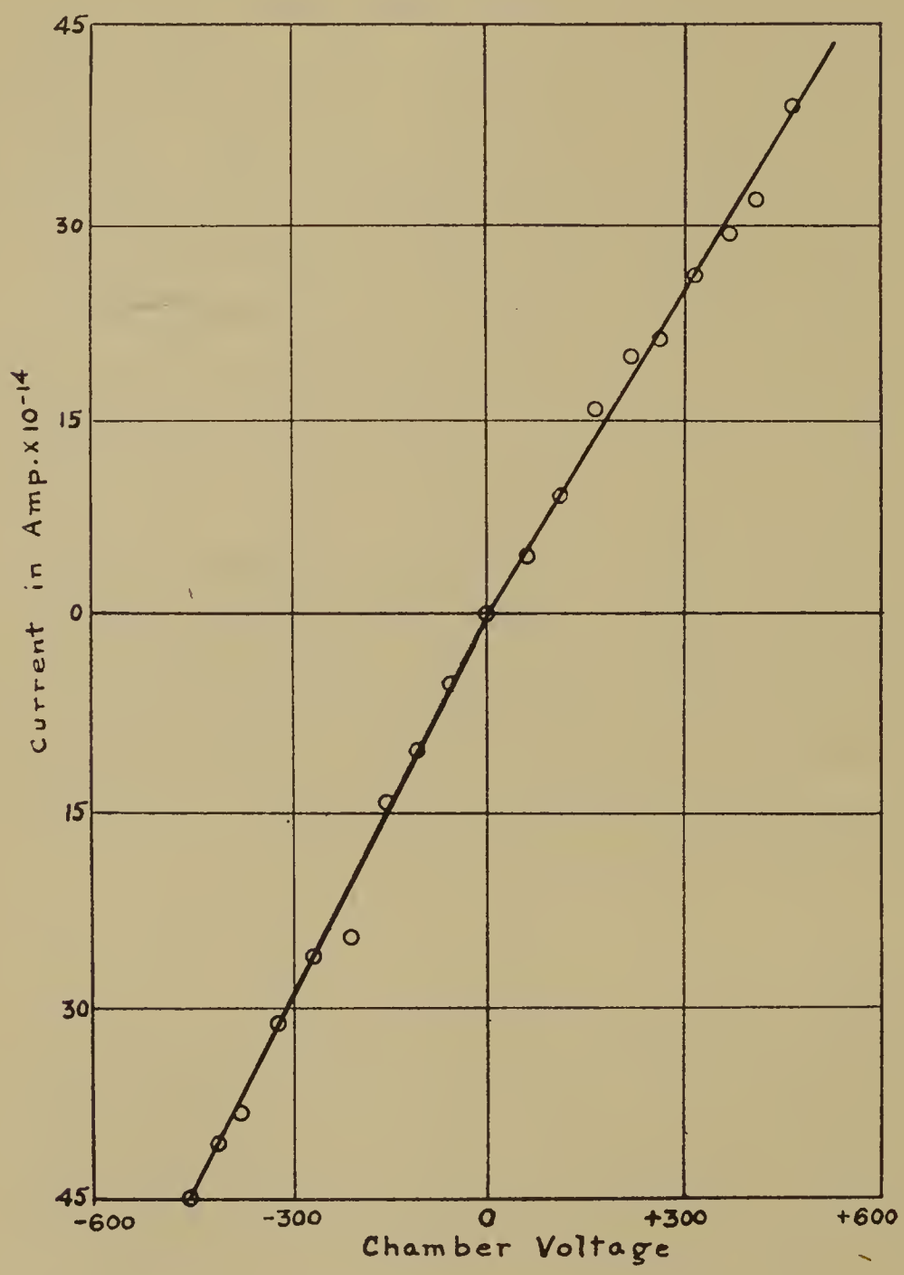

FIG. 2

Fig. 4 was constructed from the data of Fig. 3. It shows that current is directly proportional to voltage when the number of molecules reacting per unit of time is constant, and provides a further check for the data of Fig. 2.

The linear relation between voltage and current is interesting. No evidence of a saturation current could be detected, although in

an attempt to find it the voltage was pushed to as high a value as was consistent with accuracy, and the quantity of chemical action was made as small as possible. In ordinary work with photo-electric experiments, a potential gradient of 30 v. is sufficient to remove all the ions and give a saturation current, which cannot be increased with further increase of voltage. The fact that in these experiments no indication of a saturation current could be found,

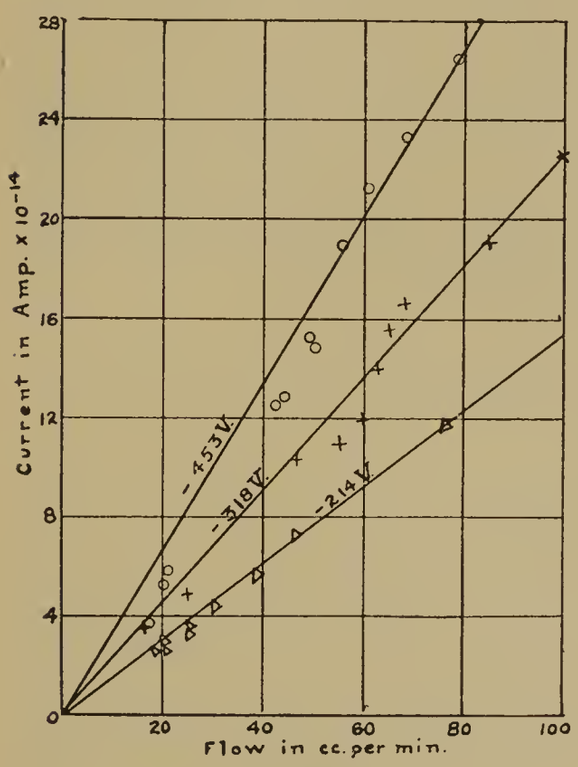

FIG. 3

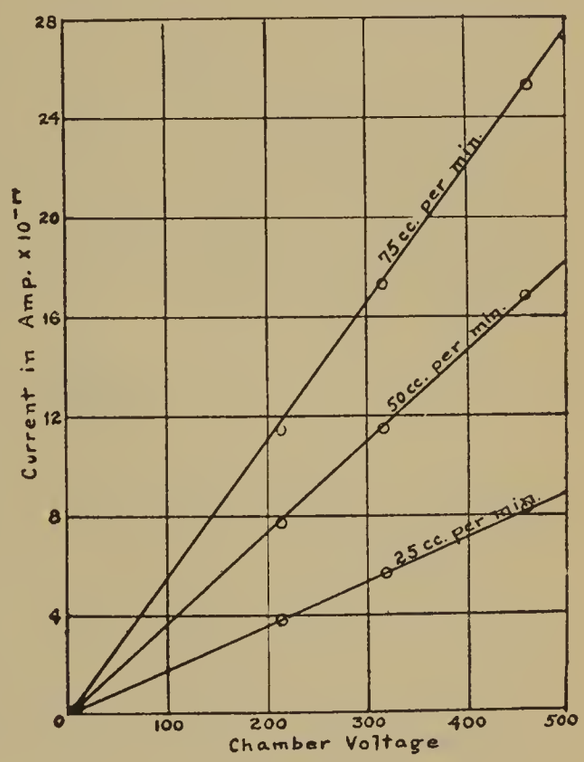

FIG. 4

even at 453 v. per cm., may indicate that recombinations of ions in the reacting gases are very rapid. If each atom of nitric oxide or oxygen in the process of chemical reaction is capable of neutralizing an ion, the rate of recombination of ions would be vastly greater than in gases which are ionized by radio-active materials or other means and contain a relatively small number of ions.

CALCULATIONS.

It would be a matter of considerable interest to determine the ratio of the number of reacting molecules to the number of ions formed, and compare this ratio with the ratios found by Lind in reactions induced by α-ray bombardment. Unfortunately, it is not possible to do this because the saturation current cannot be

determined. It is possible however to calculate the number of molecules reacting in the electrical field, and to calculate from the ionization current a *minimum* number of ions.

The oxygen was passing through the chamber at the rate of 650 cc. per min. and the nitric oxide flow was 50 cc. per minute or 0.83 cc. per sec. for a representative experiment. The total gas flow was then 700 cc. per min. or 11.7 cc. per sec. Since the cross section of the gas space in the chamber was 5.66 sq. cm. the velocity of the gases was 2.05 cm. per sec. As the electrode chamber was 10 cm. long each molecule of gas was within the electrical field for a period of 4.85 sec. Nitric oxide entered the chamber at the rate of 0.83 cc. per sec. and nearly all of this (approximately 90 per cent) was oxidized during the first 4.85 sec. At room temperature this corresponds to 2×10^{19}

$$\left(= \frac{0.8}{24{,}000} \times 6.06 \times 10^{23}\right)$$

molecules of NO reacting per second.

The number of oxygen molecules reacting was one-half as great or 1×10^{19}. The total number of molecules reacting per second within the field was therefore 3×10^{19}. The number of electrons or ions of single charge reaching the electrode was readily calculated. While 3×10^{19} molecules were reacting every second, a current of 1.7×10^{-13} amp. was passing through the gas space when the potential was 453 v. per cm. Since one electron carries a charge of 1.59×10^{-19} coulombs, it was easy to calculate that 1×10^{6}

$$\left(= \frac{1.7 \times 10^{-13}}{1.59 \times 10^{-19}}\right)$$

electrons or singly charged ions were reaching the electrode each second. Under the conditions of the experiment then, only one ion reached the electrode for every 3×10^{13}

$$\left(= \frac{3 \times 10^{19}}{1 \times 10^{6}}\right)$$

molecules reacting. It is interesting to calculate that if each molecule reacting had given rise to one free electron, and each

electron or resulting ion had succeeded in reaching the electrodes without recombination, a current of 4.75 amp. would have resulted. ($3 \times 10^{19} \times 1.59 \times 10^{19}$).

This very low ratio of ions to reacting molecules can be explained in a number of ways, and three hypotheses seem worthy of discussion.

First it may be assumed that all the reacting molecules are in a state capable of giving ionization when placed in an electric field, but that only those in the immediate neighborhood of the electrodes ever reach the electrodes. The vast majority of reacting molecules are situated farther away from the electrodes, and give ions which immediately recombine without effect on the electrometer. As the voltage is increased the thickness of this shell of ions which reach the electrodes before recombination increases.

A second hypothesis to account for the low ratio of ions to reacting molecules is based on probabilities. It may be assumed that all the ions formed are drawn to the electrodes, and that a saturation current would result except for the reason that increasing the voltage increases the number of ions. On the basis of this hypothesis it would be assumed that only occasionally in the oxidation of nitric oxide would the electron systems be in such a configuration that the potential gradient could drive out an electron, but at higher voltages more electron systems are in a state from which an electron can be expelled. For any given voltage the ratio of ions to reacting molecules would give the fraction of reacting molecules in a certain condition of instability from which an electron can be loosened.

A third hypothesis depends on a photo-electric effect at the electrodes. On the basis of the radiation hypothesis of chemical action[8] it is conceivable that blue or ultra violet light might be emitted in the oxidation of nitric oxide, and that this might drive out photo-electrons from the platinum electrodes. A careful search has been made in this laboratory[9] for such an emission of light but no blackening of a photo graphic plate through a quartz window was found, even after an exposure to the reacting gases for two days. If it was a photo-electric phenomenon which was

[8] W. C. McLewis, J. Chem. Soc. **113**, 471 (1918); Perrin, Ann. de Physique, **11**, 5-108 (1919).

[9] G. L. Sehon "A Search for the Emission of Light in Certain Chemical Reactions" Bachelor's Thesis, 1921, University of Wisconsin.

being measured, evidence of a saturation current would be expected, but as already mentioned the current was directly proportional to voltage throughout the whole range studied.

The evidence presented here is insufficient to decide just what is the true mechanism involved in the conductance of a reacting mass of nitric oxide and oxygen gases. The experiments are being extended to different reaction chambers and to other reacting gases.

DISCUSSION.*

S. C. LIND[1]: These painstaking experiments and the thorough discussion by the authors leave little room for comment. It will be interesting to increase the potential further to see whether saturation current will be reached or approached, or whether electrons and ions continue to be drawn to the electrodes in direct proportion to the potential applied. This may afford a decision between the first and the second hypothesis.

It is also well to keep clearly in mind that there is no necessary relation between chemical action produced by ionization and ionization produced by chemical reactions. Even if the truth of the former were thoroughly established, it is not a reason for predicting the latter, in fact rather the opposite. As the writers have indicated in their first hypothesis, the greater the affinity for free ions or electrons by the components of a given reaction, the smaller the chances of their reaching the electrode. J. J. Thomson's classical photochemical experiment with $H_2 + Cl_2$ still remains the stumbling block in the way of speculation in this direction.

F. O. ANDEREGG[2]: The rate of reaction between oxygen and nitric oxide is slow. This indicates that there are only a very few molecules sufficiently active to react.

H. B. WAHLIN[3]: It seems essential in this work that voltages higher than 400 be used. If it is true that by increasing the

* In the absence of the authors the above paper was presented by H. B. Wahlin.

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[2] Dept. of Chemistry, Purdue Univ., Lafayette, Ind.

[3] Dept. of Physics, Univ. of Wisconsin, Madison, Wis.

voltage there is a tendency to creep farther up on the distribution curve, you would expect that with sufficient voltage the straight line relation would no longer hold. That is, there are more free electrons or ions produced and, as a consequence, the current is greater with a tendency for it to increase more rapidly than it does. This condition would probably be attained considerably before you reach such a potential as would result in ionization by collision.

FARRINGTON DANIELS (*Communicated*): Dr. Lind has emphasized the importance of the nature of the gases and their ability to trap electrons. Only in case this dragging down of the electrons and ions is negligible would a simple M/N ratio be expected. We have found that nitrogen peroxide is a very efficient trapper of electrons, and we have tried to repeat these experiments with ionized oxygen of sufficient ozone concentration to leave no nitrogen peroxide, but only nitrogen pentoxide. Perhaps the nitrogen pentoxide will not trap the electrons as completely and will allow a greater number to reach the electrodes, resulting in a larger current.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 28, 1923, Dr. Colin G. Fink in the Chair.

RELATIONS BETWEEN SUPPLIED ENERGY, SPECTRAL INTENSITIES AND ALTERATIONS IN DIFFERENT MEDIA.[1]

By L. Hamburger.[2]

Abstract.

The conception of the unity of optical, chemical and energetic relations laid down in the quantum theory, and the Rutherford-Bohr interpretation of atomic structure, does not admit an essential difference between chemical and physical changes. The proportionality to the supplied electrical energy, shown both by the intensity of spectral lines and the pressure difference due to the transference of ponderable ions, confirms the view that atoms both receive and emit energy in quanta. Dislocated, that is, excited or partially ionized, atoms play important parts in the explanation of electroluminescence, effects observed on collisions between slow electrons and atoms, spectra not electrically excited, catalytic phenomena, and reaction velocities. Regarding the latest category by way of example the dependence of the reaction temperature on the nature of the metal carbonate used, in the cyanide process for the fixation of nitrogen, is explained with the aid of the ionizing and resonance potential data for the alkali and alkaline earth metals.

RELATIONS BETWEEN SUPPLIED ELECTRICAL ENERGY AND SPECTRAL INTENSITIES IN GASES.

K. Ångström[3] applied the bolometer to the establishment of the relation between the supplied energy and the total radiation as well as between the supplied energy and the optical radiation transmitted through an alum plate from the positive column.

[1] Manuscript received July 25, 1923. Abstracted by Duncan MacRae.

[2] Managing director of the Netherlands nitrogen fixation works, Dordrecht, Holland.

[3] Ann. d. Phys. **46**, 493 (1893).

He found them both in direct ratio to the supplied electric current. Later investigations, particularly those of the Münster school (working under the direction of H. H. Konen) have subjected definite lines and bands of different gases to a closer photometric examination with a similar result. The author, using the photographic method indicated by Holst and Hamburger[4], obtained results for simple gases[5] that showed for every spectrum line (except the argon spectrum) or band that the emission is always proportional to the supplied energy. From these results and a consideration of data on the negative glow, the luminescent arc discharge, and the single line spectrum, it is concluded that in general there is, in widely differing kinds of electric discharges in gases, always proportionality of the occurring radiation and electrochemical or photochemical reactions with the supplied energy, provided the variables are kept within those limits in which the character of the bearers (luminescence centers) remains unmodified. In mixtures of gases, for which chemical action is conceivable, chemical action takes place at electrical discharge, which action always manifests itself also spectrographically.

RELATIONS BETWEEN VARIATIONS OF PRESSURE IN SPECTRUM TUBES AND SUPPLIED ENERGY.

Small pressure differences occurring in the electric discharge in gases at pressures below 0.1 mm. have been discussed by Stark[6] and Wehnelt and Frank[7]. Remarkably enough, there is nothing to be found in the literature about differences of pressure occurring in spectrum tubes at continuous current discharges when the gas pressure is in excess of 0.1 mm. The author found in this case not only very strong effects, but also variations of pressure, which were of opposite sign compared with those found by Stark and Wehnelt and Franck, that is, the pressure increased at the anode and decreased at the cathode. This pressure effect will be called "positive pressure" effect in contradistinction to the "negative pressure" effect of Stark, and

[4] Proc. Amsterdam **20**, 1021 (1917).
[5] L. Hamburger, Diss. Delft 1917: Z. f. wiss. Phot. **18**, 1-44 (1918); Proc. Kon. Ak. v. Wetensch. Amsterdam **20**, 1043 (1917).
[6] Boltzmann Festschrift (1904).
[7] Verh. d. deutsch. phys. Ges. **12**, 444 (1910).

can with high current density amount to more than 30 per cent of the total pressure.

It should be borne in mind that to produce the positive pressure effect through mass-transportation, only the difference in number of molecules arising at the cathode and the anode through discharge of ponderable ions must be taken into account. If for simplicity we at first assume only univalent ponderable ions to be present, and only one kind of either sign, since $\frac{md^2x}{dt^2} = e\,X$ we have $\frac{n_1 eX\lambda_p}{2m_p c_p}$ positive and $\frac{n_2 eX\lambda_n}{2m_n c_n}$ negative ions passing per second through the cross section of the path of the current; n_1 and n_2 represent the number of ponderable ions of each kind per cc., e the charge, m_n and m_p the mass of the ions, X the electric force, λ_n and λ_p the free path of the ponderable ions, and c_n and c_p their mean velocities.

When on discharge every positive ion gives a_1 and every negative (ponderable) ion a_2 gas molecules, the number of gas molecules at the cathode will diminish per unit of time by

$$\left(\frac{n_2 e\lambda_n a_2}{2m_n c_n} - \frac{n_1 e\lambda_p a_1}{2m_p c_p}\right) X \qquad (1)$$

from which it follows that the difference in pressure must be in direct ratio to the potential gradient X.

Since the real conditions are much more complicated than if only univalent ions were present, it is better to write for (1):

$$X.\ \phi\ (n, a, \lambda, m, c\ .\ .\ .\ ) \qquad (2)$$

Lenard[8] took the difference in mass of the colliding particles into account. The proportionality is also found in his conduction formula. Cf. Townsend[9].

All these formulæ have been derived on the assumption of elastic collisions. In reality an important part of the collisions is inelastic and causes dislocation, ionization, recombination and radiation. The reasoning given by the author elsewhere[10] renders

[8] Ann. d. Phys. 28, 3, 312 (1900).
[9] Marx' Handbuch d. Radiologie I, 70 ff.
[10] Proc. Amsterdam 25, 467 (1922); cf, also note 3 Z. f. Electrochem. 29, 137 (1923).

it probable that the proportionality with X holds in stationary states even under those circumstances.

From the fact that a gram molecule of an ion yields a definite known quantity of gas on neutralization at an electrode, another expression for mass transportation has been derived[11] (for the case that the nature of the ions and the ratio of their numbers does not vary with the current density), in which the volume displaced by the electric mass transportation in a gas per unit of time is put equal to bAQ/p cc. of gas measured at the pressure p, A and Q representing current density and cross section of the conductor. Since expression (2) shows that the proportionality factor b must be directly proportional to X, we can write

$$q_1 = \beta \frac{AQX}{p} \tag{3}$$

Since after the stationary state has been established, $q_1 = q_2$, the quantity of gas which flows back under the established pressure difference, and since

$$q_2 = \triangle p . \phi (p, T, Q, L \ldots .) \tag{4}$$

we may write

$$\triangle p = \beta \frac{AQX}{p . \phi (p, T, Q, L \ldots)} \tag{5}$$

When the discharge takes place in a cylindrical tube whose diameter is small in comparison with the mean free path of the particles

$$q_2 = \frac{\gamma D^4 p . \triangle p}{\eta L} \tag{6}$$

and when the diameter is comparable with the mean free path according to Knudsen[12] and Langmuir[13]

$$q_2 = \delta \sqrt{\frac{T}{M}} . \frac{D^3}{L} \triangle p \tag{7}$$

The two following formulæ then result from (6) and (7) in combination with (3):

$$\triangle p = \alpha \frac{AX}{p} . \frac{L}{Q} . \sqrt{M} \tag{8}$$

[11] Proc. Amsterdam 23, 385 (1920).
[12] Ann. d. Phys. 28, 76, 799 (1909).
[13] Gen. Elec. Rev. 19, 1063 (1916).

and

$$\triangle p = \alpha AX \cdot \frac{L}{D} \sqrt{M} \qquad (9)$$

in which α is a constant resulting from β, γ and δ.

The data of the author[14], Skaupy[15], and Rüttenauer[16] have served to test these[17] equations and they have been found to be approximately valid within the following limits:

$\triangle p/p$	1.3	to	50.0
Q	0.03	to	2.0
p	0.15	to	1.2
AQ	0.66	to	12.7
X	0.6	to	45.0
M	4.0	to	40.0
L	5.0	to	60.0

It has been found that the constant α, the value of which can be of importance for the optical efficiency of a luminous gas, is different for different gases. Within the range of validity of the formulæ, it can be concluded that the nature of the luminescent centers and the current conducting ions is essentially constant. The nature of the calculation shows that the pressure effect can assume considerable values only for current densities large compared with those usual in spectroscopy.

The agreement between experimental and calculated pressure effect confirms the presence in a predominant degree of negative electrons in the path of the current; but is in contradiction to the general assumption that, at least in the inert gases, no ponderable negative ions are present in the discharges[18]. If it is possible to tear an electron from the exceedingly stable electron configuration about the nucleus, it should certainly also be possible to add an electron. Since there is a relation between the energy of combination and the radiating energy, it may well be imagined that the liberation of the energy at the relinquishment of the added electron only causes radiation of great wave length, hence loss of energy, from the point of view of luminous efficiency, in the form of heat.

[14] Diss. Delft. 1917; Z. f. wiss. Phot. **18**, 1-44 (1918); Proc. Kon. Ak. v. Wetensch. Amsterdam **20**, 1043 (1917).

[15] Verh. d. D. phys. Ges. **19**, 264 (1917).

[16] Z. f. Phys. **10**, 269 (1922).

[17] Proc. Amsterdam **25**, 463 (1922); cf. also note 3 Z. f. Elektrochem. **29**, 137 (1923).

[18] Cf. f.i.R. Seeliger Pos. Säule Marx' Handbuch d, Radiologie III, 73 ff. (1916).

QUANTITATIVE AND SIMULTANEOUS PARALLELISM OF LIGHT EMISSION AND PRESSURE EFFECT.

In connection with the results described above, it is of interest to point out that the quantum theory manifests its simultaneous and quantitative validity with regard to light emission and pressure effect by the positive column.

Indeed, we are dealing here with two typical cases of the application of the quantum theory: Light emission, involving the return of electrons from abnormal to less abnormal paths; and pressure effects, involving collisions between electrons and atoms, the formation of ions, and hence the transference of atom-electrons from the normal to the abnormal paths. When the "bearers" (luminescence centers) change their character, that of the light emission and the pressure effect also change. The latter may reverse its sign; the change of the former is illustrated by the well known "law of displacement" of Kossel-Sommerfeld[19].

If on the other hand, the electric conditions do not vary their character, if the character of the bearers remains unchanged, the experiments of the author and of Rüttenauer show the simultaneous quantitative proportionality of light and pressure effects with the supplied energy. That the light emission does not change its character by increase of the supplied quantity of energy was to be expected from the quantum theory; but the fact that the same thing applies simultaneously for the pressure effect is a contribution to knowledge. It confirms the view that the atoms both receive and cede energy in quanta and at the same time an interaction between the two effects manifested in an allied field of research, for example Klein and Rosseland's[20] theory and van der Bijl[21]. Compare also Compton[22].

DISLOCATED ATOMS. PHYSICO-CHEMICAL UNITY.

Dislocated atoms, or excited atoms, are characterized by the movement of one of the "outer" electrons in an abnormal path. These dislocated or partially ionized atoms play important parts in the explanation of such varied phenomena as electro-lumines-

[19] Ber. d. D. Phys. Ges. **21**, 224 (1919).
[20] Z. f. Phys. **4**, 46 (1921).
[21] Phys. Rev. **10**, 546 (1917).
[22] Cf. Compton, Phys. Rev. **15**, 476 (1920).

cence, effects observed on collisions between slow electrons and atoms, spectra not excited by electricity, catalytic phenomena, reaction velocities, photochemical effects. Thus we are justified in saying that the results of modern theoretical and experimental researches appear to make possible the development of a grand unity of the physico-chemical world image, in which dislocated conditions in multiform varieties, in quantous interaction with available energies, fulfill a vital function[23].

SOME POINTS OF VIEW WITH REGARD TO LUMINOUS EFFICIENCY AND ELECTROCHEMICAL PROCESSES.

The greatest efficiency in light production has been reached with luminescence radiators (Bremer's luminescent arc discharge). If the effect of the applied electrical energy is confined to the displacement of only one of the outer electrons, the return of this dislocated electron renders the energy quantitatively in the form of radiated energy, which if it be of the proper wave length will result in a great luminous efficiency. Similarly, if in endothermal electrochemical processes the process can be conducted so that a great deal of the energy is utilized for a definite chemism, the foundation has been laid for a technically efficient (electro-) chemical process. This parallelism between luminous and chemical efficiency is illustrated in the spectra of nitrogen-hydrogen mixtures, in which with high ammonia concentration the intensity of the group of ammonia bands $\lambda = 3360$ Å. U. exceeds even the neighboring nitrogen band $\lambda = 3371$ Å. U.[24]

The light emitting insects radiate energy entirely in the visible region, the maximum coinciding with the maximum sensibility of the human eye. This energy is derived from assimilated food and its radiation furnishes an example of chemo-luminescence that takes place practically quantitatively. Since in temperature radiators the efficiency diminishes rapidly with diminished energy supply, and in electro-luminescence losses at electrodes, series resistance, etc., play a more and more important part in smaller

[23] Abstractor's note: The section on dislocated atoms has been very briefly abstracted because much the same subject is discussed by K. T. Compton in another paper in this symposium.

[24] L. Hamburger, Chem. Weekbl. 15, 936 (1918).

units, there is no doubt that future development of small sources of light will advance in the direction of chemo-luminescence.

For large units our hopes remain fixed on electro-luminescence radiators. In order to avoid the consumption of energy by processes which do not contribute to light radiation, we will have to select media which are not subject to chemisms which may be of importance for electro-technical processes, but not for luminous ones. With this in mind, it is not surprising that calcium fluoride in Bremer's lamp and neon in the Moore-Claude light have played a prominent part; for calcium fluoride is perhaps the most stable of all chemical compounds and neon is one of the most inert gases. Gases having a small value for the constant α are desirable and the intimate connection of the ionization potential with undesired (electro-) chemical reactions should be kept in mind.

In general the greatest luminous efficiency is obtained when the current conduction through the ponderable particles is as small as possible. The greater the disturbance in the atoms, the smaller the chance of light emission in the visible part of the spectrum.[25] Energy applied to make an electron more than optically free is always partially lost to light emission. For this reason as a rule ideal efficiency is not to be expected from direct chemo-luminescence. In nature, probably a chemical action supplies the energy which is quantitatively used for the excitation of activated states. This conception is identical with that of Baly and his collaborators based on the inverse action: the photosynthesis in nature.

CHEMICAL REACTION AND ACTIVATION POTENTIAL.

As an example of the significance of the ionization potential in chemistry, the following reaction[26] will be discussed:

$$MCO_3 + 4C + N_2 = M(CN)_2 + 3CO$$

Bucher[28] divides the reaction into two stages:

[25] In the well known equation $h\nu = eV$, ν attains such a value in cases of violent collision that the radiation becomes displaced to the ultra-violet region of the spectrum.

[26] Hamburger, Proc. Amsterdam June, 1923; Bucher, J. Ind. Eng. Chem. 9, 233 (1917); Thorssell, Z. f. angew. Chem. 33, 251 (1920).

[27] *loc. cit.*

$$\text{I.}\quad MCO_3 + 2C = M + 3CO$$
$$\text{II.}\quad M + 2C + N_2 = M(CN)_2$$

Reaction I is exceedingly endothermal, while reaction II is strongly exothermal and takes place practically instantaneously. Reaction I may be divided as follows:

$$\begin{aligned} &a\ldots\ldots\ldots MCO_3 = MO + CO_2 \\ &b\ldots\ldots\ldots MO = M + O \\ &c\ldots\ldots\ldots O + C = CO \\ &d\ldots\ldots\ldots C + CO_2 = 2CO \end{aligned}$$

of which a and b only vary with the nature of M, and b claims the lion's share of the supplied energy.

If, in accordance with the Bohr theory, the valence electron in the metal oxide molecule is at the disposal of the oxygen and metal atom only in a characteristic "abnormal" path, we may assume that the activation necessary for the occurrence of the cyanizing reaction consists of the complete transfer of the valence electron to the oxygen atom, manifesting itself in the formation of ions. Thus it is possible that the dissociation of the metal oxide does not take place by the direct process of the splitting up of $MO = M + O$, but that on increase of energy first an *activation* sets in, manifesting itself as formation of ions.

It is known that the ionization potential of the vapor is decisive for the detaching of an electron from a free metal atom. Where it is probable, in connection with the appreciable volatilities of the metal oxides at the reaction temperatures, that the primary reaction takes place in the gas phase, we will first of all see how far the ionizing potential of the metal atoms in volts v governs the reaction temperature T in deg. K. For this purpose values of v/T are given in line 4 of Table I. The value of the reaction temperature of CaO is taken from the communication by P. Schlapfer[28], and the values of the ionization potential from a summary given by Franck.[29] It is seen from the fourth line of the table that v/T has the same order of magnitude throughout.

Considering the widely divergent circumstances the agreement may even be called remarkable, the more so as a perfectly, sharply defined reaction-temperature can not be expected on theoretical

[28] Schweiz. Chem. Ztg. **29**, 30 (1919).
[29] Phys. Z. **22**, 413 (1921).

ground. The ionization potential determines the energy required to detach entirely an "outer" electron from its normal path. Since we have concluded that in the compound the electron in question is present in an abnormal path, the conclusion is obvious that not v, but a smaller value v—v′ can give a measure of the critical supply of energy, in which v′ is a value (dislocation potential) which determines the difference of energy between the electron in the abnormal path of the compound and the electron in the normal path in the free atom.

TABLE I.

	Li	Na	K	Rb	Cs	Mg	Ca	Sr	Ba
T	1370	1200	1100	970	870	2100?	1900	1670	1320
v.....	5.4	5.1	4.3	4.2	3.9	7.6	6.1	5.7	5.2
$\frac{v \times 10^3}{T}$	4.2	4.0	4.2	4.2	4.3	3.2?	3.2	3.4	3.9
v″	1.84	2.09	1.60	1.55	1.38	2.70	1.88	1.79	1.56
$\frac{(v - v'') \times 10^3}{T}$	2.5	2.5	2.5	2.7	2.86	2.3?	2.2	2.3	2.7

We can then write in place of v/T = k as shown to be approximately true in the above table, v—v′/T = k or e(v—v′)/T = k, in which (v—v′) is called the activation potential, e the charge of the electron and e(v—v′) the "critical" activation energy. There is an analogy between v′ and the excitation potential v″, the value which determines the energy required to transfer an "outer" electron from the normal to the first abnormal path.

From the values of the relation v—v″/T recorded in line 6 of the table, it is seen that the difference between the alkalies and the alkaline earths is smaller than in line 4. In the case of the strong electropositive character of barium where, moreover, the difference between the first and second resonance potentials (2.2—1.6 = 0.6 v.) is smaller than for any of the other alkaline earth metals considered here, it is not improbable that the abnormal path in the compound corresponds more closely to the

abnormal path indicated by the second resonance potential of the metal vapor than to that indicated by the first. Accordingly, if we introduce the value 2.2 in place of 1.56, we obtain the value 2.3 for $[(v—v'') \times 10^3]/T$. The agreement of this value with the others for the alkaline earths leaves nothing to be desired.

With the aid of the Rutherford-Bohr atomic model, we have endeavored in the above to give an example of the view that, at least in definite cases, ionization and dislocation potentials are not only decisive with regard to the possibility of reaction, but also with regard to reaction velocity and reaction temperature.

Perrin believes that photochemical action occurs in every chemical reaction. Our insight into the structure of the atom makes us realize that the fundamental feature is the displacement of the electrons in it. This displacement may be brought about not only by radiation, but also in various other ways. Accordingly, it is not justifiable to assign merely a part to light in the explanation of chemical action; other forms of energy also enter. In connection with the conception of an interaction between the different forms of energy, a derivation, though only a formal one, seems possible for the relation

$$\text{activation potential} \div \text{reaction temperature} = \text{constant},$$

based on the laws of radiation. In this case the directing lines given by Tolman[30] and Rideal[31] should be taken into account. In agreement with Tolman-Rideal and in opposition to Perrin, we assume for this purpose not that one characteristic line or band is absorbed, but that the whole black radiation must be taken into account. In the calculation we then follow the path indicated by Rideal in his theoretical derivation of Trouton's law, and in the equation $e\,(v—v') = h\nu$ we let ν equal the value for the frequency ν_m (corresponding to the temperature T) in which the emission of the black radiation is a maximum. Since $\nu_m = \frac{c}{\lambda_m}$ and according to Wein's displacement law $\lambda_m T = \text{constant}$, it follows that $(v—v')/T = \text{constant}$.

It is clear that the first derivation retains its value independent of this latter derivation. The only thing we derived from Wien's

[30] J. Am. Chem. Soc., 42, 2006 (1920).
[31] Phil. Mag. 42, 156 (1921).

law is that activation energy divided by T is constant. The determination of this energy by v—v′ and the derivation of the values v and v′ are only possible by the Bohr-Rutherford atomic conception, and the characteristic frequencies of the *discontinuous* metal luminescence spectrum. It is self-evident that a similar derivation on the basis of Wien's law which is valid for *continuous* black temperature radiation only is excluded. Not until the laborious investigations by Franck have been further extended may the theory here presented only in outline be turned into a solid foundation for chemistry.

CONCLUDING REMARKS.

In the latter part of this communication we have no longer confined ourselves to the territory of the electrochemistry of gaseous conduction. A complicated type of reaction, involving solid, liquid and gaseous phases, in which the steps of the reaction are generally not considered to be electrochemical, was chosen as an illustration.

This has been done intentionally. It was our purpose to show that the conception of the unity of the optical, chemical and (electro-) energetic relations laid down in the quantum theory, and the Rutherford-Bohr interpretation of atomic structure, does not admit an essential difference between chemical and physical changes.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

MULTIPLE ELECTRODE SYSTEMS,

With an Application to the Study of Current Distribution in Electroplating Baths.[1]

By A. Harold Heatley.[2]

Abstract.

From Ohm's law, a general theory is developed for current distribution in an electrolyte with n electrodes, and tested experimentally for n = 3, 4 and 5. Equations are developed, and their possible application in electroplating is discussed. Experiments in a simple case yield confirmatory evidence. Formulæ developed in a previous paper are shown to have a limited application; and a new definition of throwing power is suggested.

SYMBOLS USED.

Also See Fig. 1 and 2.

I_t ..... Current entering the system at A, and defined as the total current.

I_a, I_b, etc..... Currents within the system.

a, b, etc..... Conductances corresponding to I_a, I_b, etc.

q, r, s..... Resistances in the star arrangement. Fig. 1b.

I_1, I_2, etc..... Currents leaving the system.

E_A, E_1, etc.,.... Potentials of electrodes Parts I—III, or polarization films, Parts IV, V.

V_1, V_2, etc..... Potential differences. $V_1 = E_1 - E_2$, $V_2 = E_2 - E_3$, etc.

n..... Number of electrodes in a system. All may have different potentials.

[1] Manuscript received May 21, 1923.

[2] Niagara Electrochemical Co., Niagara Falls, N. Y.

K.....Specific conductivity of electrolyte.

R = 1/K.....Specific resistivity of electrolyte.

Dp.....Primary current distribution, *i. e.*, the ratio of current densities at the various surfaces for zero or equal polarization.

T.....Throwing power. See equations (34), (35), (36).

Ti.....Throwing power for equal current efficiencies at all cathodes.

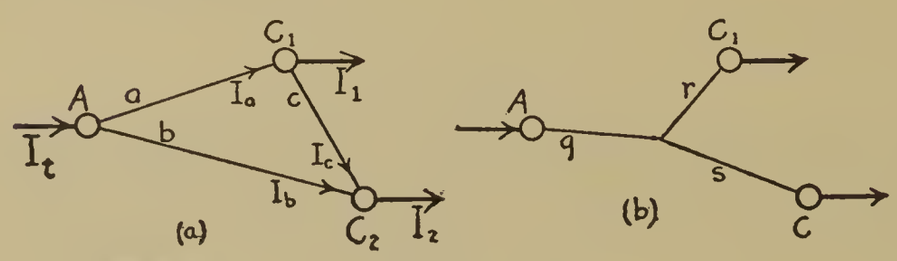


FIG. 1

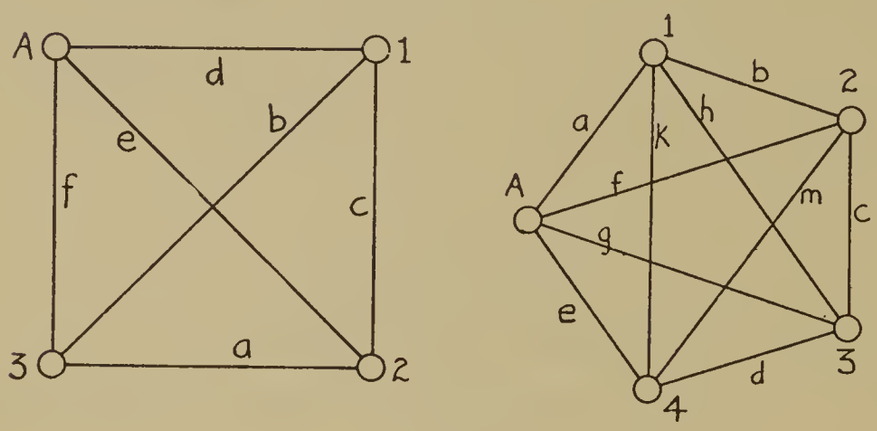


FIG. 2

I. GENERAL PRINCIPLES.

The current in a given homogeneous electrolyte between two fixed electrodes A and C_1 (non polarizable and of negligible resistance) is proportional to the potential difference applied; for the liquid at the electrode surface is always an equipotential surface, and since no current can enter or leave except by the electrodes, the lines of current flow are fixed, and Ohm's law will apply, although the current density may not be uniform over the surface of the electrode. If there is a third electrode C_2, we may divide the current I_t entering at A into two parts, I_a and I_b, which go to C_1 and C_2 respectively. Neglecting electromagnetic effects, if any, the lines of current flow for I_a thus defined, are

fixed, and independent of the potential of C_2, so Ohm's law still applies. Similarly for I_b and for I_c, the current between C_1 and C_2. The corresponding conductances may be designated as a, b, c. The currents I_1, I_2 are of course the algebraic sum of the currents in the electrolyte which reach the electrode, Fig. 1a. A mathematical proof that a three electrode system may be thus represented by a delta of conductors is given by Searle.[3]

Similar consideration of the four and five electrode systems leads to the conclusion that they may be represented by a network of conductors as shown diagrammatically in Fig. 2; similarly a system of n electrodes leads to a network of $n(n-1)/2$ conductors.

The values of the conductances in the three electrode system may be obtained by measuring with a Kohlrausch bridge (a. c. and telephone) the conductance between the three pairs of terminals successively, but the calculation of a, b, c, from these results is tedious. They are easily found by measuring the conductance between A, and C_1 joined to a common lead with C_2. This gives $a+b$; similarly $b+c$ and $c+a$; from which a, b, c can be found. For the general case, Rosebrugh[4] has shown a method of determining each conductance, which is illustrated by experiments recorded later.

II. MATHEMATICAL TREATMENT.

Knowing the values of a, b, etc., the currents I_1, I_2, etc., leaving at electrodes 1, 2, etc., may be expressed in different ways of which three are selected, *i. e.*, in terms of (I) the potentials of all the electrodes, E_A, E_1, etc. (II) the total current I_t (entering at A), and the differences of potential between pairs of electrodes along the line 1, 2, 3, etc., $V_1 = E_1 - E_2$, $V_2 = E_2 - E_3$, etc. (III) any other current (*e. g.*, the smallest) and V_1, V_2, etc. The four electrode case will serve to illustrate.

By definition

$$I_1 = I_d - I_b - I_c \qquad (1)$$

$$I_2 = I_c + I_e - I_a \qquad (2)$$

$$I_3 = I_a + I_b + I_f \qquad (3)$$

[3] Electrician, 66, 1002 (1911).
[4] Applied Science, New Series, 1, 179 (1907-08).

(I) $I_d = d(E_A - E_1) \qquad I_e = e(E_A - E_2)$ etc. (4)

$$I_1 = dE_A - (d + b + c)\,E_1 + cE_2 + bE_3 \tag{5}$$

$$I_2 = eE_A + cE_1 - (c + e + a)\,E_2 + aE_3 \tag{6}$$

$$I_3 = fE_A + bE_1 + aE_2 - (f + b + a)\,E_3 \tag{7}$$

(II) $I_c = cV_1 \qquad I_a = aV_2 \qquad Ib = b(V_1 + V_2)$ (8)

$$\frac{-I_d}{d} + \frac{I_e}{e} = V_1 \tag{9}$$

$$\frac{-I_e}{e} + \frac{I_f}{f} = V_2 \tag{10}$$

$$I_d + I_e + I_f = I_t \tag{11}$$

Solving (9) (10) (11) by determinants, and placing $S = d + e + f$,

$$I_d = \frac{dI_t - d(e + f)V_1 - dfV_2}{S} \quad \text{(Similarly } I_e, I_f) \tag{12}$$

$$I_1 = \frac{dI_t - [d(e + f) + S(b + c)]V_1 - (df + bS)V_2}{S} \tag{13}$$

$$I_2 = \frac{eI_t + (de + cS)V_1 - (ef + aS)V_2}{S} \tag{14}$$

$$I_3 = \frac{fI_t + (df + bS)V_1 + [f(d + e) + S(a + b)]V_2}{S} \tag{15}$$

(III) Writing I_t in terms of I_3 from (15) and substituting in (13) (14)

$$I_1 = \frac{dI_3 - [f(d + b + c) + db]V_1 - [bf + d(a + b + f)]V_2}{f} \tag{16}$$

$$I_2 = \frac{eI_3 + (fc - be)V_1 - [e(a + b + f) + af]V_2}{f} \tag{17}$$

These equations are still valid if any of the quantities are zero, or if the currents or voltages are negative. The same type of algebraic solution serves for the five, six, etc., electrode case.

The analogous equations for five electrodes are shown on the following page.

The equations developed above are believed to be in the simplest form possible, but in the case of the three electrode system, the algebra may be simplified by noting the well known fact that a delta of conductors may be replaced by a star arrangement[5], Fig. 1-b. For this case it is more simple to consider the resistances, $q = c/Z$, $r = b/Z$, $s = a/Z$, where $Z = ab+bc+ca$. Then the resistance $A - C_1$ is $q+r$; and $q+s$, $r+s$, are found similarly, from which p, q, r, are calculated.

$$V_1 = sI_2 - rI_1 = sI_t - sI_1 - rI_1 \qquad (29)$$

$$I_1 = (sI_t - V_1)/(r + s) \qquad (30)$$

Similarly $$I_2 = (rI_t + V_1)/(r + s) \qquad (31)$$

From (29) $$I_1 = (sI_2 - V_1)/r \qquad (32)$$

III. EXPERIMENTAL VERIFICATION.

To check the three electrode case, it is most convenient to combine (30) and (31) and write

$$I_2/I_1 = (Kr + KV_1/I_t)/(Ks - KV_1/I_t) \qquad (33)$$

where K is the specific conductivity of the electrolyte. The quantities Kr and Ks are constant for a given position of the electrode in a given bath and independent of composition and temperature.

A rectangular glass cell, 19 x 11 x 11.5 cm. was set up. Electrode A was a sheet of copper fitting snugly in one end. C_1, C_2 were copper cylinders 56.5 x 25.0 mm. diam. mounted on wood on vertical iron shafts which could be rotated. Contact was made as shown in Fig. 3. The quantity of solution used was always 1100 cc., which gave a depth of 6.0 cm., just enough to cover the electrode. The relative positions of electrodes in the cell were fixed.

Using a copper sulfate solution ($K = 0.0114$, determined in a conductivity cell) the values of q, r, s, as determined from Kohlrausch bridge conductance measurements, were 13.28, 2.285, 9.43 ohms, respectively. From these results, the graph of (33)

[5] Fowle, Handbook for Electrical Engineers (1915), Sec. 2 Art. 34.

(I) $I_1 = aE_A - E_1(a + b + h + k) + bE_2 + hE_3 + kE_4$ (18)

$I_2 = fE_A + bE_1 - E_2(f + b + m + c) + cE_3 + mE_4$ (19)

$I_3 = gE_A + hE_1 + cE_2 - E_3(c + h + g + d) + dE_4$ (20)

$I_4 = eE_A + kE_1 + mE_2 + dE_3 - E_4(e + k + m + d)$ (21)

(II) Placing $W = a + f + g + e$

$$I_1 = \frac{aI_t - V_1[a(f + g + e) + W(k + h + b)] - V_2[a(g + e) + W(k + h)] - V_3(ae + Wk)}{W} \quad (22)$$

$$I_2 = \frac{fI_t + V_1(af + Wb) - V_2[f(g + e) + W(c + m)] - V_3(fe + Wm)}{W} \quad (23)$$

$$I_3 = \frac{gI_t + V_1(ag + Wh) + V_2[g(a + f) + W(h + c)] - V_3(ge + Wd)}{W} \quad (24)$$

$$I_4 = \frac{eI_t + V_1(ae + Wk) + V_2[e(f + a) + W(k + m)] + V_3[e(a + f + g) + W(k + m + d)]}{W} \quad (25)$$

(III) $$I_1 = \frac{aI_4 - V_1[e(a+k+h+b)+ak] - V_2[e(a+h+k)+a(k+m)] - V_3[ek+a(e+k+m+d)]}{e} \quad (26)$$

$$I_2 = \frac{fI_4 - V_1(fk - be) - V_2[f(e + k + m) + e(c + m)] - V_3[f(e + k + m + d) + em]}{e} \quad (27)$$

$$I_3 = \frac{gI_4 - V_1(kg - bh) - V_2[g(k + m) - e(h + c)] - V_3[g(e + k + m + d) + de]}{e} \quad (28)$$

was plotted on I_2/I_1 and KV_1/I_t as axes. (Fig. 4) It is an hyperbola.

To check the graph, the cell was connected through resistances, as shown in Fig. 5, to the a. c. buzzer used with the conductivity bridge. R_1, R_2 (non-inductive resistances) were given suitable

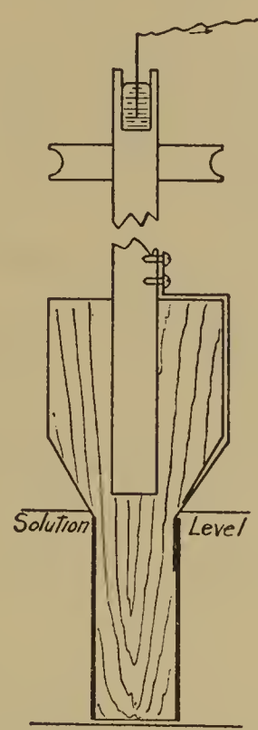


FIG. 3.

values and the slider S was adjusted to give zero or minimum sound in the telephone T. x and y are the resistances of the segments of the slide wire between R_1 and R_2.

$$\text{Then } xI_1 = yI_2 \qquad \therefore I_2/I_1 = x/y$$

Also

$$\frac{V_1}{I_t} = \frac{I_1(R_1 + x) - I_2(R_2 + y)}{I_1 + I_2} = \frac{R_1 + x - (R_2 + y)I_2/I_1}{1 + I_2/I_1}$$

A series of values from this experiment is plotted on Fig. 4, as circles. Another series using a solution K = 0.0050 is plotted as crosses. The agreement is satisfactory.

To check the validity of the network representation of the four electrode case, four platinized platinum electrodes were fixed in a vessel of tap water. The conductances were measured with the Kohlrausch bridge as before, and are recorded in Table I. The

figures in the "electrodes" column indicate the electrodes used for that measurement, *e. g.*, 12 — 3A indicates that the leads from 1 and 2 were joined as one terminal and those from 3 and A as the other terminal. The conductances a, b . . . . . f were calculated from the first six measurements as shown, and then used to calculate the last four conductances in the Table. The results

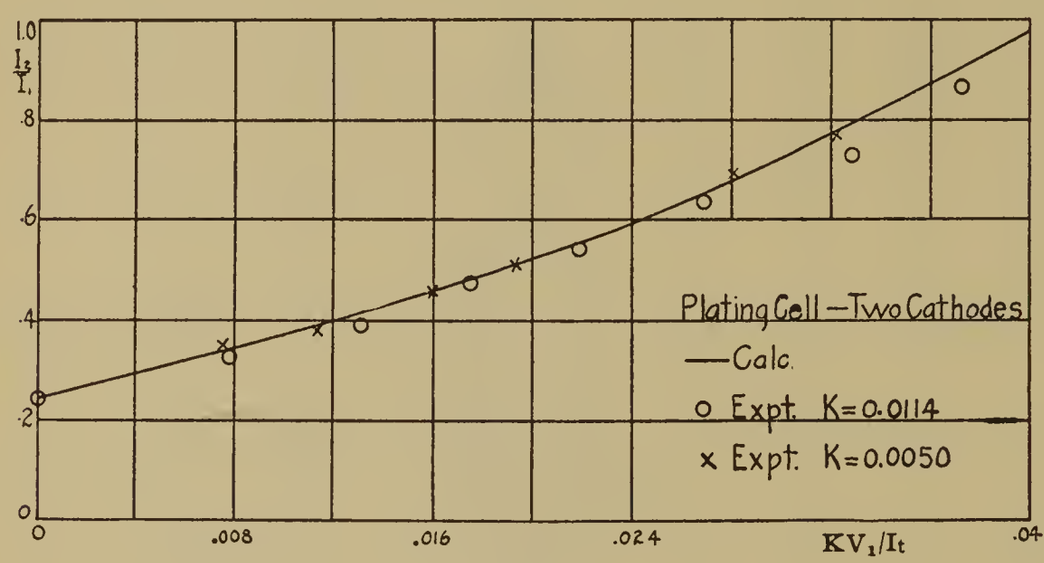


FIG. 4.

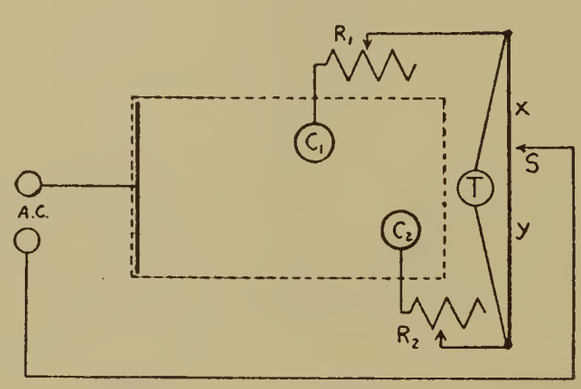


FIG. 5.

of a similar study of the five electrode system are recorded in Table II. The results in these Tables show a very close conformity with the requirements of the theory.

IV. APPLICATION TO ELECTROPLATING.

If a cathode of irregular shape is placed in an electroplating bath, the current density over its surface is not uniform, and the greater polarization at the points of greater current density "throws" the current (and thus the metal deposited by it) to

parts which would not otherwise receive as much. The surface of this cathode may be considered as divided into a number of equal areas over each of which the current density is sufficiently uniform to make the polarization equal. *The liquid at the surface of the polarization films* (F_1, F_2, etc.) over each of these areas

TABLE I.

Four Electrodes.

No.	Electrodes	Conductance		
		from diagram Fig. 2	Observed mhos	calculated mhos
1	1 — 23A	d+b+c	0.865×10^{-3}	
2	2 — 13A	a+e+c	0.925	
3	3 — 12A	a+b+f	0.605	
4	12 — 3A	a+b+d+e	0.680	
5	23 — 1A	b+c+e+f	1.250	
6	31 — 2A	c+a+f+d	1.239	
7	A — 123	d+e+f	0.770	0.773×10^{-3}
8	1 — 23	$\frac{d\,(e+f)}{d+e+f}+b+c$	0.823	0.816
9	2 — 31	$\frac{e\,(f+d)}{d+e+f}+c+a$	0.860	0.857
10	3 — 12	$\frac{f\,(d+e)}{d+e+f}+a+b$	0.451	0.447

$a = \frac{1}{2}(2+3-5) = 0.140 \times 10^{-3}$ $\quad d = 1-(b+c) = 0.194 \times 10^{-3}$
$b = \frac{1}{2}(1+3-6) = 0.116$ $\quad e = 2-(c+a) = 0.230$
$c = \frac{1}{2}(1+2-4) = 0.555$ $\quad f = 3-(a+b) = 0.349$

Also note:
[1+2+3+7] (0.003165 mhos) should equal [4+5+6] (0.003169 mhos).

may now be considered as non-polarizable electrodes to which the equations of Part II may be applied. The conductances to be used might be found by making up a cathode of the same shape from pieces of metal, insulated from each other with insulated leads for each; for the distance between the metal and the surface of the polarization film may usually be neglected.[6] If necessary the anode could be treated the same way, but the problem will

[6] Wilson and Youtz, Ind. and Eng. Chem. **15**, 603 (1923), have shown the thickness of the diffusion layer for electrodes in quiet solutions to be about 0.5 mm., and much less for stirred solutions. As the concentration is uniform outside this layer, it may for the purposes of the present paper be considered as the polarization film.

Table II.

Five Electrodes.

No.	Electrodes	Conductance		
		From diagram Fig. 2	Observed mhos	Calculated mhos
1	A — 1234	a+f+g+e	1.173×10^{-3}	
2	1 — A234	a+k+h+b	1.068	
3	2 — A134	b+f+m+c	1.131	
4	3 — A124	c+h+g+d	0.695	
5	A1 — 234	f+g+e+k+h+b	1.851	
6	A2 — 134	a+b+e+g+m+c	1.851	
7	A3 — 124	d+e+a+f+c+h	1.301	
8	12 — A34	a+k+h+f+m+c	0.861	
9	13 — A24	b+c+a+k+g+d	1.611	
10	23 — A14	b+f+m+h+g+d	1.654	
11	4 — A123	d+m+k+e	0.993	0.995×10^{-3}
12	A4 — 123	a+f+g+d+m+k	1.235	1.232
13	14 — A23	a+e+b+h+d+m	1.803	1.807
14	24 — A13	c+d+b+f+k+e	1.825	1.826
15	34 — A12	e+k+m+c+h+g	1.192	1.192
16	34 — A1	$\frac{(m+c)\ (b+f)}{m+c+b+f}+g+h+e+k$	1.142	1.143
17	31 — 24	$\frac{(a+g)\ (f+e)}{a+g+f+e}+b+c+d+k$	1.413	1.415
18	A — 123	$\frac{e\ (k+m+d)}{e+k+m+d}+a+f+g$	0.961	0.953
19	1 — A24	$\frac{h\ (c+g+d)}{h+c+g+d}+a+b+k$	1.061	1.060

$a = \frac{1}{2}(1+2-5) = 0.195 \times 10^{-3}$ $\quad c = \frac{1}{2}(3+4-10) = 0.086 \times 10^{-3}$
$f = \frac{1}{2}(1+3-6) = 0.226$ $\quad e = 1-(a+f+g) = 0.468$
$g = \frac{1}{2}(1+4-7) = 0.284$ $\quad k = 2-(a+h+b) = 0.128$
$b = \frac{1}{2}(2+3-8) = 0.669$ $\quad m = 3-(b+f+c) = 0.150$
$h = \frac{1}{2}(2+4-9) = 0.076$ $\quad d = 4-(c+h+g) = 0.249$

Also note: $3 \times [1+2+3+4+11]$ (*i. e.* 0.015180 mhos) should equal $[5+\ldots\ldots+10+12+\ldots+15]$ (*i. e.* 0.015182 mhos).

be simplified here by considering its polarization film as a single electrode, F_A.

In applying the equations, E_A, E_1, etc., are the potentials of F_A, F_1, etc., above any arbitrary zero (*e. g.*, the potential of the cathode metal); V_1, V_2, etc., are the differences of potential be-

tween F_1 and F_2, F_2 and F_3, etc. (Consider the surfaces numbered in the order of their distances from the anode, 1 being the nearest.) But these E's and V's are themselves functions of the I's which are expressed in terms of them. Their values will be such as to correspond in the appropriate equation.

In a recent paper, Haring and Blum[7] have reviewed the literature on throwing power and discussed the subject thoroughly. In the legend for Fig. 1 of their paper the term "effective" resistance is used without any definition or explanation being given. From their equations (3) and (4) we may make the definition (using the notation of this paper)

$$\text{(Effective) } R_1 = E_1/I_1. \quad \text{Similarly } R_2 = E_2/I_2 \qquad \text{(A)}$$

In developing their equations, they assume that R_2/R_1 is a constant, regardless of the values of I_1 and I_2. Writing down the values of R_1 and R_2 from equation (A) and Fig. 1b, we have

$$R_1 = E_1/I_1 = \frac{q(I_1 + I_2) + rI_1}{I_1} \qquad \text{(B)}$$

$$R_2 = E_2/I_2 = \frac{q(I_1 + I_2) + sI_2}{I_2} \qquad \text{(C)}$$

$$\frac{R_2}{R_1} = \frac{I_1}{I_2}\left(\frac{q(I_1 + I_2) + sI_2}{q(I_1 + I_2) + rI_1}\right) \qquad \text{(D)}$$

$$\text{When } I_1 = I_2,\ R_2/R_1 = (2q + s)/(2q + r) \qquad \text{(E)}$$

$$\text{When } I_1 = 2I_2,\ R_2/R_1 = (6q + 2s)/(3q + 2r) \qquad \text{(F)}$$

Equations (E) and (F) show that in general, R_2/R_1 is dependent on the ratio I_1/I_2, though it is a constant in their apparatus for which $q = 0$, $r = R_1$, $s = R_2$.

Haring and Blum[7] state two objections to the type of arrangement used by Horsch and Fuwa[8], and by Arndt and Clemens[9], both of which approximate the conditions in a plating bath. The first objection is not sustained; in the case of the two cathode apparatus, the primary current distribution Dp[10] is readily meas-

[7] Trans. Am. Electrochem. Soc. 44, 313 (1923).
[8] Trans. Am. Electrochem. Soc., 41, 366 (1922).
[9] Chem. Ztg., 46, 925 (1922).
[10] Dp is suggested to replace the symbol K used by Haring and Blum.

urable by making the resistances A-C_1 and A-C_2 two arms of a Kohlrausch bridge (high frequency a.c. and telephone), the other two arms of the bridge being the two segments of a slide wire. Dp is s/r; this could also be obtained by finding a, b, c by the method of Part I, since a/b = s/r. For the more general case, the primary ratio is the ratio of the conductances leading from the anode to the various cathodes; *e. g.*, for the four cathode case (Fig. 2) Dp = a : f : g : e, the values of which can be found by the method of Roseburgh[4] illustrated in Tables I and II. The second objection is quite valid but the apparatus can be modified until the current density is sufficiently uniform to give an approximation, as in the present paper.

Haring and Blum[7] recommend a definition which may be stated thus (dropping the per cent factor)

$$\text{Throwing Power (T)} = (Dp - M_1/M_2)/Dp \qquad (34)$$

where M_1, M_2 are the weights of metal deposited per unit area on near and distant surfaces of the cathode.

This definition is open to the objection that when T reaches its maximum value (*i. e.* when M_1/M_2 reaches its minimum value of unity) it has a value depending on Dp. If we define T *as the actual deviation of the metal distribution ratio from the primary current distribution divided by the maximum possible deviation,* thus

$$T = (Dp - M_1/M_2)/(Dp - 1) \qquad (35)$$

we have an indication as to whether the throwing power is approaching its maximum value, which is unity and does not depend on Dp.

The significance of the definition in (34) as applied to commercial plating where a certain thickness is required on the distant surface (as discussed by Haring and Blum[7] Part III) does not hold where the change is, for example, from 10 to 30 per cent instead of from 0 to 20 per cent throwing power, if the calculation is based on the metal deposited at 10 per cent throwing power. It seems therefore, that there is little to lose in changing to the new definition.

When three or more cathodes (or parts of one cathode) are

being considered, the definition in (35) cannot include all the information. A study of the four cathode case could be reported thus

$$T = \frac{M_1 : M_2 : M_3 : M_4}{a : f : g : e} \qquad (36)$$

In a given numerical case it would be preferable to adjust the successive ratios, so that both M_1 and a had the value 100; or both M_4 and e had the value unity, *e. g.*

$$T = \frac{100 : 80 : 60 : 40}{100 : 70 : 40 : 20} \qquad (36a)$$

or

$$\frac{2.5 : 2 : 1.5 : 1}{5 : 3.5 : 2 : 1} \qquad (36b)$$

If it becomes desirable to consider specially two of the cathodes, *e. g.*, the second and third, (35) and (36a) might be used thus:

$$T^2_3 = \frac{3.5/2 - 2/1.5}{3.5/2 - 1} = 0.555 \qquad (35a)$$

Writing Ti for T when the current efficiencies at the near and distant surfaces are equal (*e. g.*, in acid copper solutions over a wide range of current densities) (35) may be rewritten,

$$Ti = (Dp - I_1/I_2)/(Dp - 1) \qquad (37)$$

Combining (33) and (37) and introducing s/r for Dp

$$Ti = \frac{(Kr + Ks)\ KV_1/I_t}{(Ks - Kr)\ (Kr + KV_1/I_t)} \qquad (38)$$

The significance of Kr and Ks is noted under (33). (38) like (33) is an hyperbola.

Haring and Blum[7] Part VI discuss a case requiring a relation with I_2 instead of I_t. From (32)

$$I_1/I_2 = s/r - V_1/rI_2 = Dp\ (1 - V_1/sI_2) \qquad (39)$$

which may be expanded to

$$I_1/I_2 = Dp\left(1 - \frac{1}{Ks} \times \frac{KV_1}{I_2}\right) \qquad (40)$$

Combining (37) and (40)

$$Ti = \frac{1}{Ks - Kr} \times \frac{KV_1}{I_2} \qquad (41)$$

Plotted on axes I_1/I_2 (or Ti) and KV_1/I_2, (40) and (41) are straight lines. Compare (33) and (38).

Equations like (33) can be derived in the case of more than two cathodes (*e. g.*, by combining (24) and (25). The equation in the case of n cathodes will be of the form

$$\frac{I}{I} = \frac{Rp_1 \pm R^2p_2^2 \times V_1/RI_t \pm \ldots \pm R^2p_n^2 \times V_{n-1}/RI_t}{\text{a denominator of the same form as the numerator}} \qquad (42)$$

where R is the specific conductivity of the electrolyte; p_1 is a conductance; and p_2^2, p_3^2, etc. are terms of conductances of the second power. Like Kr and Ks, Rp and R^2 p^2 are constants; V/RI_t is analogous to KV/I_t. If (42) is the ratio of the currents to the

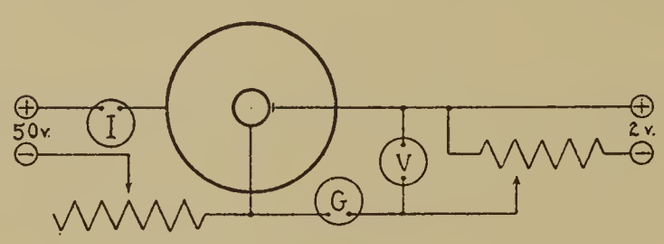


FIG. 6.

nearest and to the most distant surfaces, the signs in the numerator are all minus and those in the denominator are all plus. (42) is a general confirmation of the conclusions of previous investigators that the *current ratio* (and thus the *throwing power*) *is dependent on* (a) *rate of change of cathode potential with current density* (on which V/I_t depends) and (b) *the resistivity of the solution,* R.

The application of the equations above, to the prediction of current distribution in the two cathode case is discussed below. For the three cathode case using a similar graphical method, it would be necessary to plot two surfaces on two three-dimensional

graphs, both having V_1/RI_t and V_2/RI_t as horizontal axes, and the vertical axes being I_1/I_2 for one graph and I_1/I_3 (or I_2/I_3) for the other. For the four cathode case, graphical methods are inapplicable, and the prediction would be a long tedious process. It would probably be easier to set up an apparatus and measure the throwing power; and if the current distribution were also desired, four ammeters and three balancing resistances could be inserted in the circuit—an extension of the principle illustrated in Fig. 10.

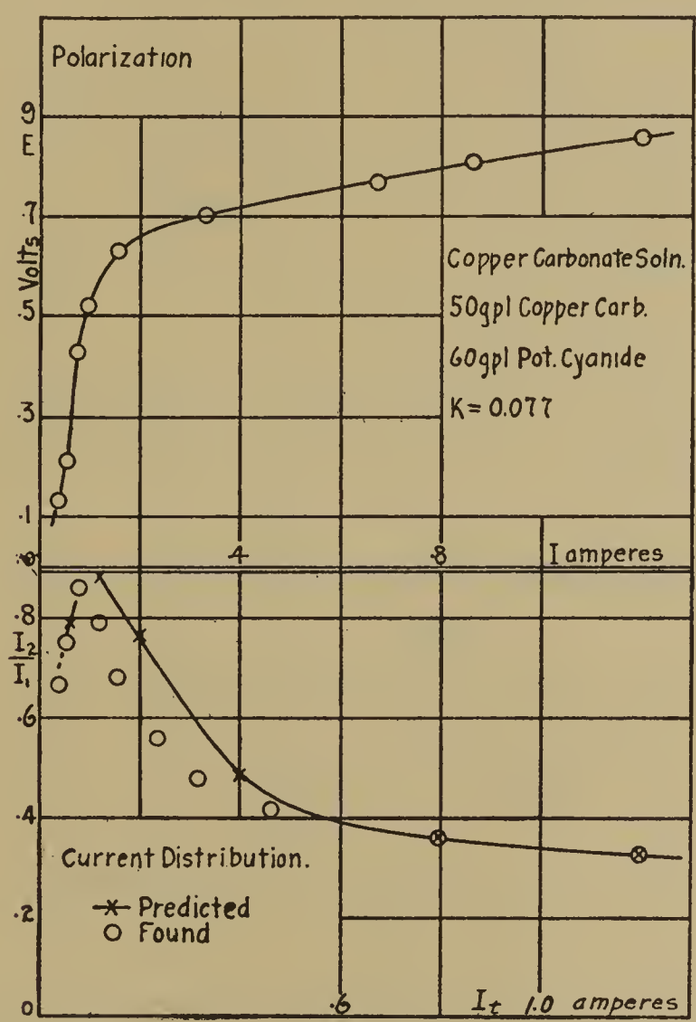


FIG. 7.

V. EXPERIMENTS.

To verify the application of these equations, it is necessary to have the cathode polarization curve. A cylindrical glass vessel was used in which a cylindrical sheet of copper formed the anode. One of the cylindrical copper cathodes was mounted centrally in this and rotated at 480 ± 20 r. p. m. The polariza-

tion was measured between the cathode and an auxiliary electrode, consisting of a tip of copper wire held about 1 mm. from the cathode by a glass tube into which it was sealed with wax. This voltage was read on a 3-volt meter, using a potentiometer arrangement, Fig. 6. The curve for a solution of copper potassium cyanide (commercial chemicals) at room temperature is shown in

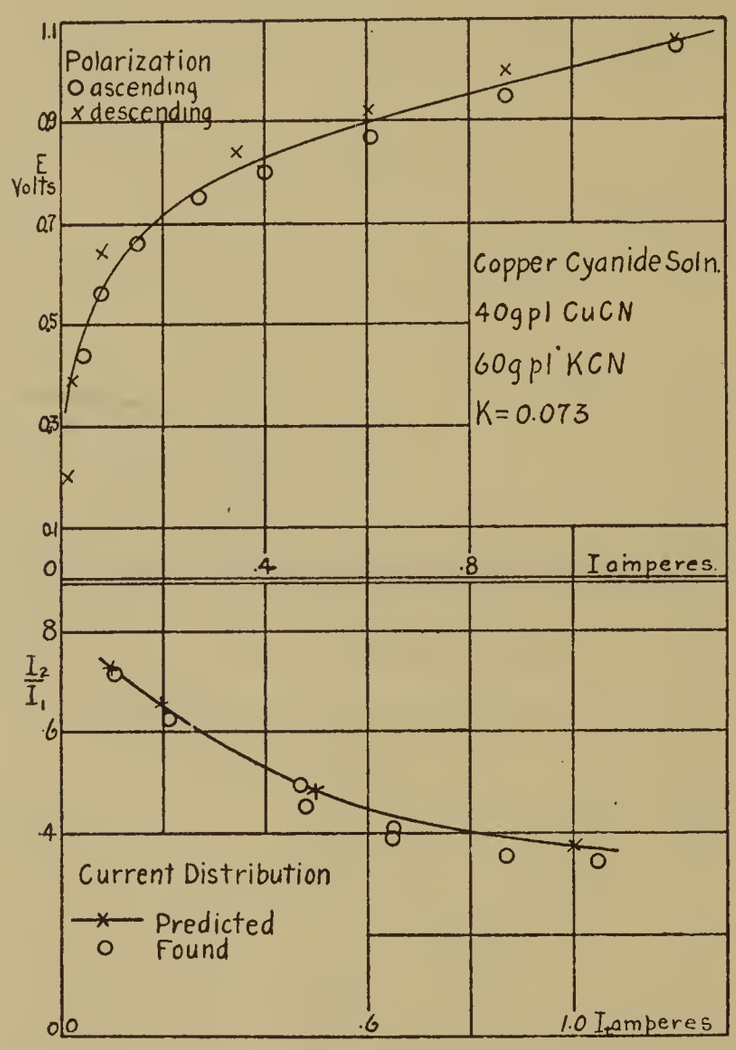


Fig. 8.

Fig. 7. Fig. 8 is a similar curve. As noted by Haring and Blum[7] it is difficult to secure reproducible results; Fig. 9 shows two curves obtained with the same solution on the same day, the condition of the metal surface being as nearly alike as possible.

With this information, we can predict the current distribution for these solutions in the rectangular cell with the cathodes placed as before, by introducing the assumption that the polarization is the same over the whole surface of each cathode, and equal to that measured in the cylindrical cell; though we know that this is

not strictly correct. We may use the graphs of (33), (40), (39) or (41); but the latter two are inconvenient for (37) must be used to get I_1, which is necessary to find V_1. Since (33) (Fig. 4) is already plotted it will be used. The computation proceeds by approximations.

Consider the curve of Fig. 8. First take $I_t = 0.5$ amp., assume $I_2/I_1 = 0.43$ whence $I_1 = 0.35$ amp., $I_2 = 0.15$ amp., and $E_1 = 0.81$ v. $E_2 = 0.665$ v. *i. e.* $V_1 = 0.145$ v. and $KV_1/I_t = 0.0212$. This value, when plotted on the graph of (33), is seen to be too low. Now try $I_2/I_1 = 0.515$, whence we find KV_1/I_t

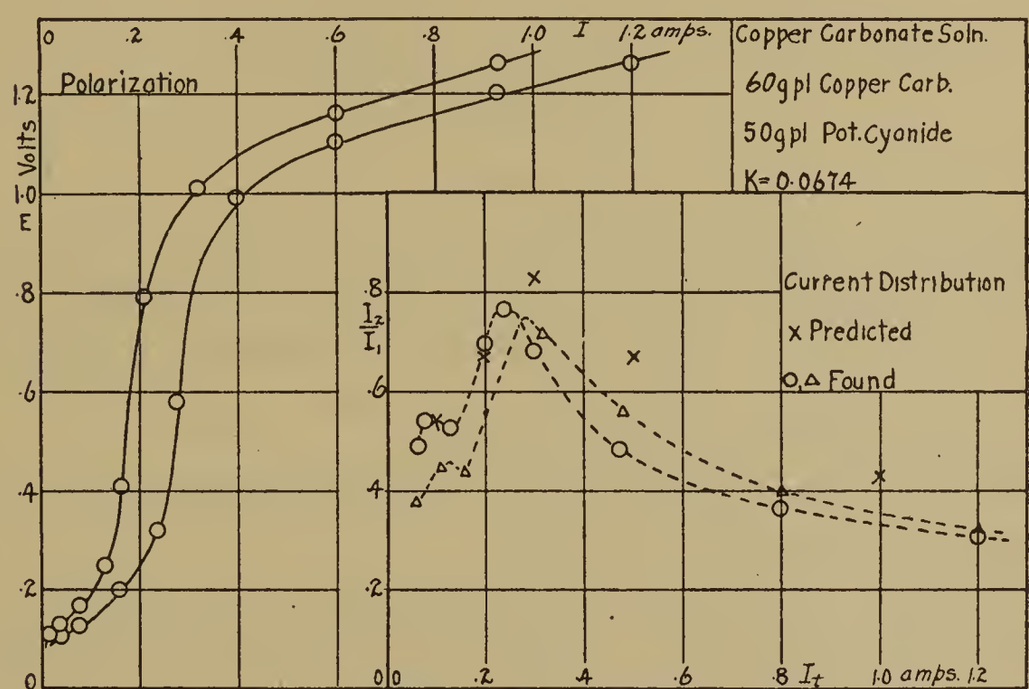


FIG. 9.

$= 0.0160$, which is too high. Interpolation gives $I_2/I_1 = 0.49$ Similarly for other values of I_t. These predicted values are plotted in Fig. 8. Predictions are also made and plotted on Fig. 7 and 9, the latter being based on the higher polarization curve there. The maxima in Fig. 7 and 9 are caused by the inflection in their polarization curves.

To test the accuracy of these predictions, the apparatus was arranged as in Fig. 10, where G is a galvanometer connected across the two cathodes which were kept at the same potential by moving the slider S. The ammeters measured the currents I_2 and I_t from which I_2/I_1 was calculated: The temperature and

the rate of stirring was the same as when the polarization was determined. As will be seen from Fig. 7, 8 and 9, in which the predicted values of I_2/I_1 are compared with those directly determined, the method of prediction employed yields results in conformity with the experiments.

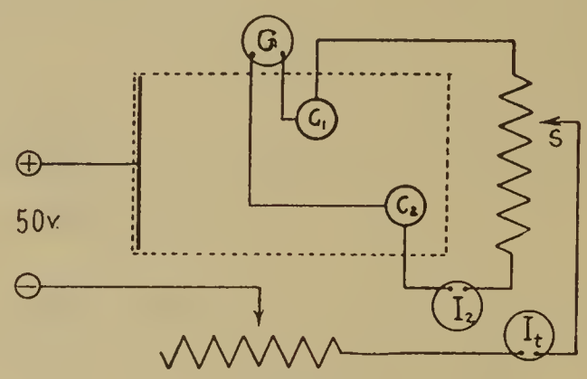


FIG. 10.

SUMMARY.

The theory developed states that an electrolyte with n electrodes is equivalent to n(n—1)/2 conductors connecting each electrode with every other electrode. A method is shown by which the value of these conductances may be determined by n(n—1)/2 conductance measurements.

Equations are developed relating currents, conductances, and potentials or differences of potential.

The theory is verified by experiments when n = 3, 4, 5.

When the equations are applied to electroplating, the significance of the quantities involved is pointed out.

Experiments with a simple electroplating bath confirm the validity of this application of these equations.

My sincere thanks are tendered to Professor W. Lash Miller, Professor T. R. Rosebrugh, and Professor J. T. Burt-Gerrans for their interest and assistance in this work, which was carried on in the Electrochemical Laboratory of the University of Toronto during the winter of 1922-23.

DISCUSSION.

WM. BLUM[1]: In the paper on "throwing power" presented at the spring meeting by H. E. Haring and myself, numerous assump-

[1] Chemist, Bureau of Standards, Washington, D. C.

tions were made and arbitrary definitions employed, in order to simplify the apparatus and method. Mr. Heatley has given a more rigid demonstration of the current relations in a multiple electrode system. It is doubtful, however, whether in the present state of the plating industry, direct use can be made of these formulæ. It would be desirable for purposes of illustration to indicate the order of magnitude of the difference in ratios for a given simple case, depending upon whether it was computed from these rigid formulæ or by our admittedly approximate methods.

In our comments upon forms of apparatus used previously, we indicated that in them the ratio could not be "readily" computed, that is from simple length measurements. Probably it could be measured with a potentiometer.

It is difficult to get an even approximately uniform current density upon cathodes arranged as in the papers referred to by us. In Mr. Heatley's paper, the actual current densities on the rotating cylinders must have been far from uniform, even though the deposit of metal may have been nearly uniform, owing to the rotation.

Any definition of "throwing power" is arbitrary and should therefore be made as simple as possible. Mr. Heatley's suggested definition is slightly more complicated than ours, but has the advantage that it indicates the relation of the improvement in ratio to the maximum possible improvement in a given arrangement. As, however, the "throwing power" by either definition varies with the primary ratio, the latter must always be stated, and the more simple definition is equally significant.

A. H. Heatley: The equations of the present paper or those developed by Haring and Blum will give the same results when applied to their apparatus.

To apply equation (8) (Haring and Blum) to the apparatus described in the present paper, which more nearly conforms to the conditions in a plating bath, we need to know E_f ($= I_f R_f$). However, it is shown in equation (C) (Heatley) that R_f (*i. e.* R_2) depends on the values of q and s, which are quantities not recognized by the mathematics of Haring and Blum.

With the solution described in Fig. 8, the resistance of my cell (anode to two cathodes) is 2.36 ohms. Dp = 4.127, so a

consideration of Fig. 1 (Haring and Blum) would lead us to calculate $R_n = 2.94$ ohms, $R_f = 12.11$ ohms. Using these data and the Fig. 8 polarization curve with equation (8) (Haring and Blum) we find $I_n/I_f = 3.5$ approx., when $I_n + I_f = 0.5$ amp. The value shown in Fig. 8 is $I_n/I_f = 2.04$ (*i. e.*, 1/0.49). For the former $T_i = 0.20$; for the latter $T_i = 0.68$ approx.

Carl Hering[2] (*Communicated*): The author has asked me to discuss his paper from the standpoint of the forces developed electromagnetically in the liquids, which may move them, as I had made a special study of such forces.

My researches were confined, however, practically entirely to liquids in furnaces in which the current densities are enormous as compared with those in electrolysis. All this class of mechanical forces increase with the square of the current, hence while they may be (and are in fact) quite formidable in resistance furnaces, they are probably quite small in electrolysis. On the other hand an aqueous solution is far more easily moved by small forces than the heavy liquid metals, hence such forces, which are undoubtedly always present, though small, might cause appreciable motions which might be made good use of.

The best general guide concerning these forces is to remember that the lines of magnetic flux which encircle every current carrying conductor tend to contract like stretched rubber bands, with the important difference, however, that the more they contract the stronger the contracting force gets. Hence they tend to crush the conductor radially; this is called the pinch effect. This tends to make the material flow toward the central axis, and if this force is any less than at other parts of the circuit (which is generally the case) the material will move into those parts.

These flux lines also repel each other, and if they are supposed to be attached in some way to the particles of the material of the conductor through which the current is flowing (which appears to be true according to the modern electronic theory, and is borne out by experiments and has not been disproved) this repulsion will tend to stretch the conductor. This has been called the stretch effect.

When a circuit turns a corner the flux lines are far more dense

[2] Consulting Electrical Engineer, Philadelphia, Pa.

on the inside of the corner than on the outside; and where they are more dense their mutual repulsion will be greater. Hence this force tends to straighten such a conductor and produces a sort of churning at the corner. This the writer many years ago called the corner effect; others later called it the motor effect.

In general, some such forces exist whenever and wherever there is any difference in flux density, especially when this difference is abrupt. They act to move those particles in which the current which is producing the flux flows, as though they were attached to them. When such a force is spent by doing work, it is immediately replaced by the current, hence (unlike strains in springs and rubber bands) they act continuously like a valveless pump, as the forces do in a centrifugal pump.

A discussion of such forces, their experimental demonstration and their theories will be found in a paper by the writer on Electromagnetic Forces, J. Am. Inst. Elec. Eng., Feb., 1923, p. 139.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society, held in New York City May 3, 1923, G. B. Hogaboom in the Chair.

THE INFLUENCE OF THE BASE METAL ON THE STRUCTURE OF ELECTRODEPOSITS.[1]

By W. Blum[2] and H. S. Rawdon[3]

Abstract.

It is shown that if copper is deposited electrolytically upon cast or rolled copper which has been cleaned with alkali, the structure of the base metal does not apparently affect that of the electrodeposit. If however the surface of the base metal has also been treated with nitric acid, the electrodeposited copper possesses both the crystal form and orientation of the base metal.

In any consideration of the structure of electrodeposited metals, or of the mechanism by which definite structures are produced, it is necessary to take into account the possible effect of the structure of the base metal. In 1916, Geo. B. Hogaboom[4] called attention to the probable existence of such effects. Recently it was definitely stated by H. J. S. Sand[5] that "The microstructure of a non-electrolytic copper plate has however no influence on subsequent electrolytic metal deposition." Similarly W. E. Hughes[6] says "If a piece of metal be taken, say, copper, that has an obviously crystalline structure, and deposits of the same metal, copper, be formed upon it, the crystals of the base metal do not grow. No instance of such growth has ever been observed."

At the meeting of the American Electrochemical Society in September, 1921, in a discussion of a paper on the structure of

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Manuscript received January 31, 1923.

[2] Chemist, Bureau of Standards, Washington, D. C.

[3] Physicist, Bureau of Standards, Washington, D. C.

[4] Trans. Am. Electrochem. Soc. 29, 369 (1916).

[5] Fourth Report on Colloid Chemistry. Dept. Sci. and Ind. Res. British A. A. S., London 1922, p. 353.

[6] Electrodeposition of Iron, Bull. 6, Dept. Sci. and Ind. Res., London 1922, p. 36.

alternately deposited metals,[7] Mr. Hogaboom[8] called attention to a point overlooked by the author of that paper, *viz.*, that in one of the photographs the structure of the rolled copper of the base metal was reproduced in the electrodeposit.

In order to determine whether such an effect can be consistently produced, a few experiments were made by us, in which copper was deposited under specified conditions upon strips of copper having definite structures. The results which are here reported show clearly that under certain conditions the microstructure of electrolytic copper is a direct continuation of the structure of the base copper. Further investigations will be required to determine whether and under what conditions the structure of an electrodeposit may be influenced by that of a base metal of dissimilar composition.

The four specimens of copper used as base metal were as follows:

1. A sample of commercial rolled sheet copper No. 22 B. & S. gauge.
2. A piece of sample 1, which was annealed by heating to 500° C. for 15 minutes in an electric oven.
3. A piece of sample 1, which was subjected to a 4 to 1 reduction in thickness by cold rolling it between steel rolls.
4. A piece of cast copper cut from a pig of that metal, which was machined to the desired size.

Strips of the above samples, each about 3 x 10 cm., (1.2 x 4 in.) were used in the following experiments. They were first cleaned with benzene and alcohol and then by making them cathodes for about 1 minute in an electrolytic cleaner, containing about 60 g./L. (8 oz./gal.) Na_2CO_3 and 7.5 g./L. (1 oz./gal.) NaOH and 7.5 g./L (1 oz./gal.) NaCN. They were rinsed thoroughly, and the *lower half* only of each specimen was dipped for a short time into dilute nitric acid (1 : 1). The plates were again rinsed and hung directly in a copper plating bath containing 200 g./L. (27 oz./gal.) $CuSO_4 . 5H_2O$ and 100 g./L. (13 oz./gal.) H_2SO_4. They were then plated on both sides for six hours at a current density of 0.8 amp./sq. dm. (7 amp./sq. ft.). No agitation was used.

[7] W. Blum. Trans. Am. Electrochem. Soc. 40, 307, (1921).
[8] Trans. Am. Electrochem. Soc. 40, 318, (1921).

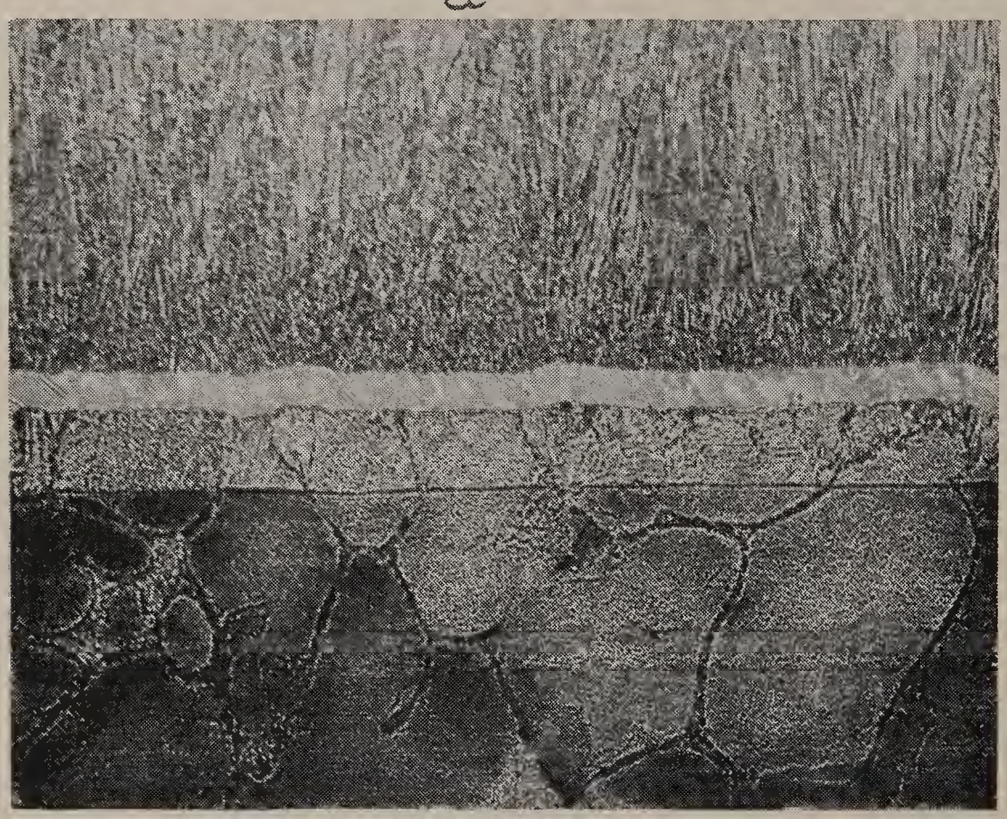
Fig. 1. Section of the chilled side of a "pig" of cast copper, upon which copper was electrolytically deposited. x 100.

a, the surface was cleaned but not pickled, prior to the electrodeposition.

b, the surface was pickled after cleaning.

The various zones indicated in "b" are the same throughout all of the micrographs: w, base metal; x, electrodeposited copper (first layer); y, electrodeposited nickel; z, electrodeposited copper (second layer).

a



b

Fig. 2. Section of cast copper from the interior of the "pig," upon which copper was electrolytically deposited. x 100.

a, the surface was cleaned but not pickled, prior to the electrodeposition.

b, the surface was pickled after cleaning.

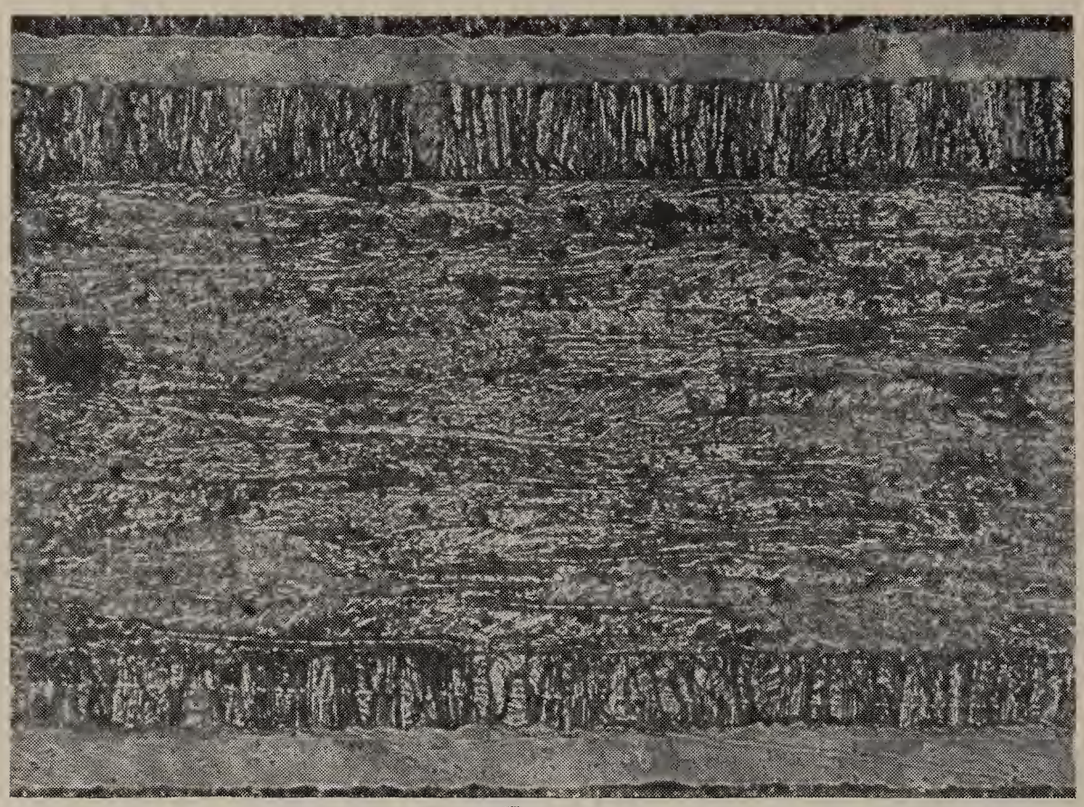
a

b

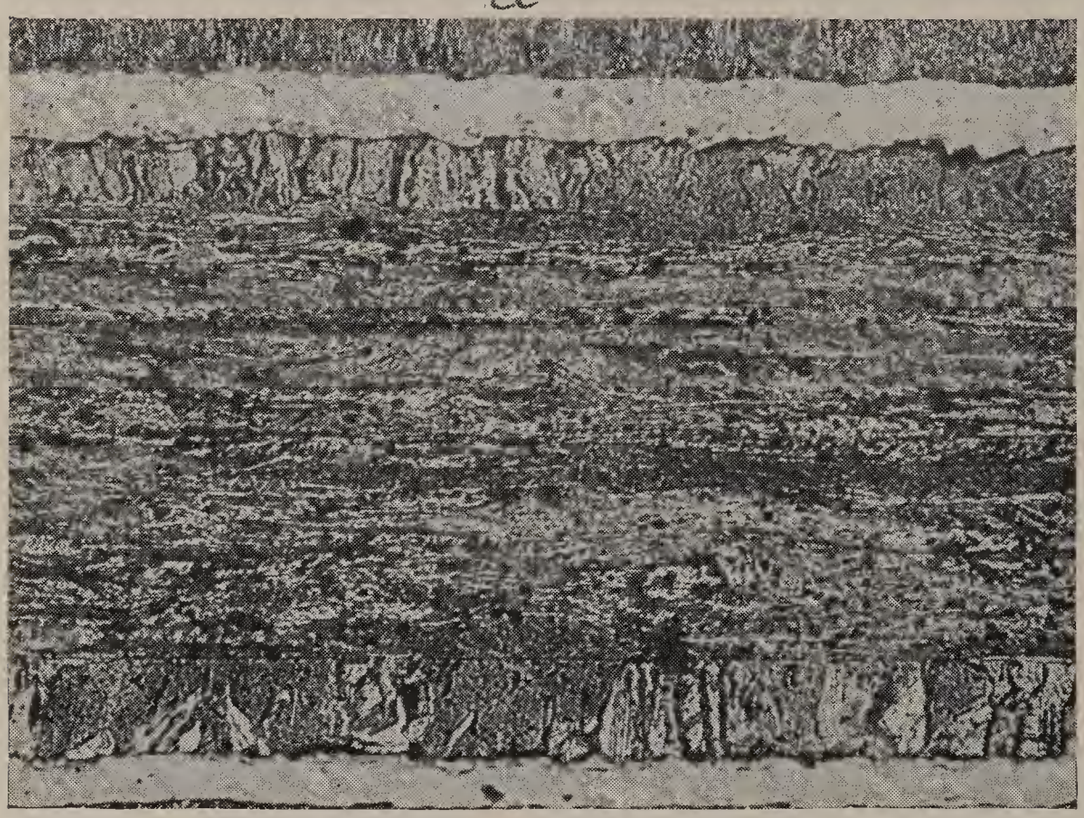
FIG. 3. Annealed commercial sheet copper upon which copper was electrolytically deposited. x 150.

a, the surface was cleaned but not pickled, prior to the electrodeposition

b, the surface was pickled after cleaning.



a



b

FIG. 4 Electrolytic copper deposited upon cold-rolled copper sheet. x 150.
a, the surface as cleaned but not pickled, prior to the electrodeposition.
b, the surface was pickled after cleaning.

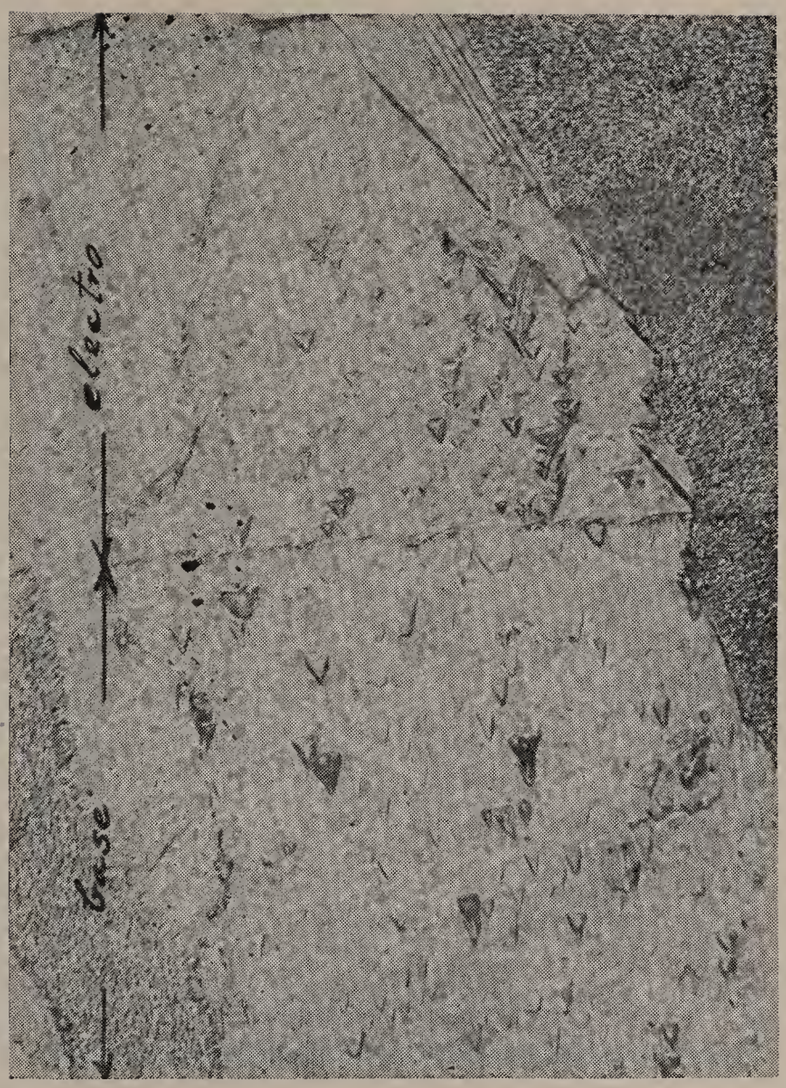


Fig. 5. Crystalline orientation of electrolytic copper relative to that of the metal upon which it was deposited. x 500.

The spot shown here is indicated by the arrow in Fig. 1. Note the continuity of crystalline orientation of base metal and electrodeposit, as shown by the etching pits.

After being copper plated the specimens were heavily plated with nickel to mark the boundary of the initial copper layer, after which they were again plated with copper under the same conditions given above in order to facilitate their subsequent mounting and polishing for microscopic examination.

Samples of each piece were mounted in a suitable holder and cross-sections were polished and etched with a mixture of ammonium hydroxide and hydrogen peroxide, after which the structure was photographed with the results shown in Fig. 1 to 4. On account of the similarity in the results obtained, micrographs of all the materials used have not been included, those of the commercial sheet (specimen No 1.) being omitted. In each of these figures, the upper picture marked "a," represents a section through the upper portion, *i. e.,* the part that had been cleaned but not pickled; and that marked "b," the lower portion, that had been cleaned and pickled.

Each micrograph represents transverse sections through the following zones or layers of metals: w, base metal (copper); x, electrodeposited copper; y, electrodeposited nickel; and z, second layer of electrodeposited copper. For the purposes of reference these zones have been indicated in Fig. 1, b.

These pictures show clearly that if the surface has been treated with acid, so that the structure of the metal is "opened up" by the removal of any buffed surface layer, the electrodeposited metal takes the structure of the base metal. If, on the other hand, the surface has been cleaned with alkali, but not with acid, the deposited copper has the customary fibrous or columnar structure of electrolytic copper produced under the conditions used.

That the electrolytic deposits have not simply the external form, but also the internal structure of the copper on which they are deposited, is evident from Fig. 5, in which is shown at a higher magnification, the portion of the specimen, shown in Fig. 1, which is indicated by the arrow in the nickel layer. In order to bring out the internal structure deeper etching was used. It is evident from Fig. 5 that the etching figures in the crystals of the electrodeposit have the same orientation as in those of the cast copper upon which they were deposited; and that therefore the electrolytic copper has actually taken the internal structure of the cast copper.

The above results are not surprising if we realize that in order for any crystalline deposit to be continuously formed, each layer of atoms must be influenced by the orientation of the preceding layer. Obviously for such growth it is necessary for the deposited metal to be in intimate atomic contact with the base metal, such as was secured in these experiments by treating the surface with nitric acid. On those specimens which were cleaned in alkali but not in acid, there may have been a layer of nearly amorphous buffed metal or else a film of hydrogen, oxygen, oxide or some other foreign material, which while not sufficient to prevent good adherence of the electrodeposited metal, did not permit the intimate contact necessary for maintaining the atomic orientation of the crystals of base metal in those of the deposit. This observation suggests as a definition of absolute cleanness of a metal surface, a condition in which the structure of the base metal may be continued by electrodeposition.

It is impossible to indicate the exact practical significance of this behavior until data are obtained upon the deposition of, *e. g.*, nickel and silver on copper, iron and brass. It is entirely reasonable to expect that, under certain conditions at least, the structure of an electrodeposit of one metal may be influenced by that of another on which it is deposited. Most of the metals have similar space lattices, and it has been shown[9] that in alloys, such as brass produced by fusion, within certain ranges atoms of zinc can replace those of copper without changing the atomic spacing. Crystal growth is especially probable between nickel and copper, or silver and gold, both pairs of which have almost identical atomic spacings. To the extent that a space lattice of a base metal is actually continued by electrodeposition there must be formed at the immediate surface of contact a true alloy. Whether such formation of alloys occurs to a measurable extent could perhaps be determined by X-ray studies.

Since, as has been shown, the structure of an electrodeposit may be influenced by that of the base metal, it will be necessary in future studies in this field to specify both the structure of the base metal and the method of preparing it before plating upon it.

The authors desire to acknowledge the assistance of J. H. Winkler and S. Epstein in the preparation and examination of the specimens.

[9] E. C. Bain. Trans. Am. Inst. Min. and Met. Eng., Feb., 1922.

DISCUSSION.

CHAS. H. ELDRIDGE[1]: Dr. Blum shows that by cleaning the surface electrolytically he gets a clean surface, but does not corrode or etch the surface, else the crystal structure would persist in the electrodeposit.

Dr. Blum claims that when an electrodeposit is made on rolled metal, that the crystal structure persists. Is this really in accordance with Fig. 4, where the cathode blank is rolled or hard-worked copper, which is not a natural copper structure but simply a mass or conglomerate of crystal fragments and amorphous metal?

It would be of interest if this test were applied to a sheet of cold-worked copper that had been just heated to the recrystallization point. I should judge from results given here that the copper plating would in that case have the same very close-grained structure.

Can the refiner of copper improve his cathode deposit by using a rolled starting sheet, an annealed blank or recrystallized blank in place of an electrolytic starting sheet? Can we avoid certain diseases of cathode, such as sprouting and treeing by so doing?

In dezincification or corrosion of condenser tubes in salt water, the zinc is taken out and a layer of copper is left. I think that we here have a means of proving whether the copper left after dezincification of condenser tubes is electrolytic or simply altered metal.

For instance, suppose we find that a fine-grained brass condenser tube, after corrosion in sea water, leaves a fine-grained copper deposit. Would this not prove that our copper was electrolytic and not secondary?

A. K. GRAHAM[2]: Regarding the last statement, a micrograph of a corroded brass condenser tube will reveal copper which is the result of electrolytic action. This is especially so where beta brass is found in the grain boundaries of the alpha brass. The former sets up an electrolytic couple with the alpha brass. Its zinc goes into solution leaving copper. This copper in turn be-

[1] Research Metallurgist, Metropolitan Museum of Art, New York City.
[2] Chem. Engr., Philadelphia, Pa.

comes negative to the alpha brass so that the latter is also attacked, its zinc dissolving, leaving the copper.

I can support Dr. Blum's findings in this paper by some of my own. The results reported here are not just unusual cases, but are more general than the writer claims.

Regarding the statement that one does not get reproduction unless the cathode is cleaned in nitric acid and then taken, after washing, directly into the plating bath, I may say that this can be varied. Reproduction can be obtained by taking copper directly from cyanide, after washing, into the plating solution. The secret of it, it seems to me, is not in the manipulation immediately before plating but in having a clean metal surface.

The reproduction is apparent in metal which was large-grained as with annealed metal. With cold worked metal one does get reproduction, and while it is not very apparent in the etching shown, yet if the metal were etched more lightly and observed at a higher magnification it would be more evident.

As long as we are starting on this particular kind of work, of the influence of base metals on deposits, a distinction should be made between what we speak of as reproduction and the influence of the base metal. It is easily apparent in the case of metal which has been annealed, where the grains are large, that the deposit completely reproduces the base metal. Now in the case of cold worked metal and other cases that have been investigated, I feel that one is justified in saying that one is getting reproduction of the surface, whatever that surface may be. If it is buffed metal, for instance, and chemically clean, it is reproduced in the deposit. The surface of buffed metal is not necessarily amorphous, but it is severely broken up and deformed so that the resulting deposit reproducing the flowed surface appears to be a new crystal growth. It is not necessarily so. All of the cases may be regarded as reproduction of the base metal surface, and they not only differ greatly in appearance depending on that surface, but the resulting deposit, after it has become thick enough to take on the characteristic electrolytic columnar structure, is influenced markedly as a result of the reproduction. There is, therefore, what one might call a primary and secondary influence, namely, reproduction and its resultant influence.

H. K. RICHARDSON[3]: In plating chromium on nickel steel, we have found that by treating with an acid bath we get better results than with cathode cleaning. But we get still better results if we have an anode cleaning of the metal before we pass into the chromium-coating bath.

When we take a microphotograph we find that in case of the anode cleaning there is no apparent spacing between the coating and the under-body; whereas, if we take plain acid treatment we find that there is a space between the coating and the under-body. I would like to know if Dr. Blum has had any experience with the anode cleaning instead of the acid cleaning.

W. BLUM: We did not make any experiments upon this point. I believe the question as to whether anode cleaning would be effective would depend upon whether the product at the anode was soluble. If the metal when used as an anode tended to become coated with an oxide, such treatment would not increase the adherence. But if that can be avoided, I see no reason why anode cleaning should not be as effective as any other method.

H. K. RICHARDSON: In the case of the anode cleaning, the adherence was great, and I know in the experience of other folks, in depositing iron on iron, they get the same result. If they use anode cleaning, the iron plating is very firmly adherent, so that you can not see where the plating joins the under-body.

G. B. HOGABOOM[4]: It is indeed a pleasure to have an opinion expressed several years ago so well confirmed. At that time the cause of a coarse crystalline deposit of silver on articles made from 18 per cent nickel silver was traced directly to the structure of the metal base. Correcting the time and temperature of annealing not only gave better plating results, but also improved the polishing of the nickel silver and the burnishing of the silver deposit. It is evident that the metallurgist as well as the physicist must work with the electro-chemist in the studying of the problems of electrodeposition. Take, for example, the work done upon the effect of addition agents. It is quite probable that many of the results obtained were materially affected by the structure of the cathode. The structure of the anode has been found to be

[3] Westinghouse Lamp Works, Bloomfield, New Jersey.
[4] Research Engr., Scovill Mfg. Co., Waterbury, Conn.

an important factor in the estimation of anode corrosion. A plater's anode which has a coarse structure dissolves more readily than one with fine crystals. In fact, the rate of corrosion can, in a great measure, be controlled by the structure of the metal used as anode.

In the study of overvoltage the structure of the electrodes should be taken into consideration if confirmatory results are to be obtained. What influence coarse or fine crystalline structure of electrodes has upon the passage of the current is not definitely known, but from some observations made it is a condition that should not be overlooked.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, G. B. Hogaboom in the Chair.

CURRENT DISTRIBUTION AND THROWING POWER IN ELECTRODEPOSITION.[1]

By H. E. Haring[2] and W. Blum.[3]

Abstract.

"Throwing power" in electrodeposition may be defined as the deviation of the actual metal distribution from the primary current distribution. It is shown mathematically and experimentally to be dependent upon (a) the rate of change of cathode potential with current density, (b) the resistivity of the solution, and (c) the cathode efficiency at different current densities. A simple apparatus for the measurement of throwing power has been developed, and applied to the study of copper sulfate and cyanide solutions.

I. INTRODUCTION.

The term "throwing power" as employed in electrodeposition may be popularly defined as that property of a solution by virtue of which relatively uniform distribution of metal is obtained upon a cathode of irregular shape. This property is of considerable technical importance in electroplating and electroforming.[4] In electroplating articles with deep recesses, such as shaving soap and tooth powder boxes, it is especially desirable to employ solutions with good throwing power, in order to coat the less accessible parts without putting an excessive amount of metal upon the other parts. In electrotyping the service of a plate

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Associate Chemist, Bureau of Standards, Washington, D. C.

[3] Chemist, Bureau of Standards, Washington, D. C.

[4] "Electroforming" is a term recently suggested by one of the authors (W.B.). It may be defined as "the production or reproduction of articles by electrodeposition," and is analogous to the German term "galvanoplasty" which has sometimes been used in English and American texts. It includes electrotyping, and the manufacture of phonograph matrices, tubes, etc., by electrodeposition.

depends directly upon the thickness of metal on the printing surface, which is determined by the proportion of the metal that is deposited in the depressions in the mold.

It is probable, as has been suggested by Foerster and others, that the same factors which determine metal distribution on a cathode also influence the structure of the deposit. In general, those conditions which give good distribution also produce smooth deposits, a relation which is obvious if we consider that to produce a smooth coating it is necessary for the metal to be deposited uniformly, and thus to fill up any minute hollows between crystals.

While the importance of this subject has long been recognized, comparatively little research has been conducted upon it, and still less application of the principles has been made commercially. The purpose of this paper is to explain and demonstrate some of the principles of throwing power, and to point out their possible commercial applications. Most of the experiments have been made with copper solutions and deposits. A few illustrations are given of the behavior of solutions of other metals. A more detailed study of the throwing power of nickel solutions is in progress.

II. HISTORICAL.

Few researches have been conducted specifically upon throwing power, and many of the data and views upon this subject are simply incidental references in general articles. It is difficult therefore to prepare an exhaustive bibliography.

Apparently W. Pfanhauser, Jr.,[5] was the first to state a relation between conductivity, cathode potentials and current distribution. He considered that the determining factor is the difference between the discharge potentials of the metal ion and of the conducting salt cation. He derived a mathematical formula from which the effects of certain changes in operating conditions were predicted, and discussed its application to brass plating solutions.

Foerster[6] explained clearly the fundamental principle of throwing power, *viz.*, that the differences between cathode potentials required to produce different current densities on two parts of

[5] Z. Electrochem. 1, 895 (1901).

[6] Elektrochemie Wässeriger Lösungen, 2nd Edition 1915, p. 423; and 3rd Edition 1922, p. 487.

any given object must compensate for the differences between the potentials necessary to overcome the ohmic resistances from the anode to these points. He gave a few general illustrations and urged a more exhaustive study of the subject.

One of the few specific researches on throwing power is that recently published by Horsch and Fuwa[7] upon zinc plating solutions. The effects of various additions, especially to zinc cyanide solutions, were determined by means of an apparatus in which the relative weights of metal deposited upon three plates, which collectively constituted the cathode, were determined. Their observations and explanations were in general in accordance with the views expressed by Foerster.

More recently some observations upon the throwing power of nickel solutions have been published by Arndt and Clemens,[8] whose results are also in accord with the principles stated by Foerster.

During the past year some interesting information has been reported independently to the American Electroplaters' Society by Geo. B. Hogaboom, and by L. M. Graham upon the distribution of metal deposits upon plane surfaces and upon irregular shapes. The observations of these authors are valuable in emphasizing the importance of determining what conditions of operation will produce most nearly uniform distribution.

III. GENERAL PRINCIPLES.

In considering the distribution of current or of metal upon a given cathode, it is necessary to distinguish between (1) the "primary current distribution," which is determined solely by the dimensions of the electrodes and the electrolyte, (2) the "secondary current distribution," which is a function of the composition of the electrolyte, and (3) "the metal distribution," which is determined by the secondary current distribution and the cathode efficiencies.

The primary current distribution is realized only when (a) there is no polarization at the cathode, (b) the polarization is equal on all parts of the cathode, or (c) when alternating current is applied, of sufficient frequency to reduce to a negligible mini-

[7] Trans. Am. Electrochem. Soc. **41**, 363, (1922).
[8] Chem. Ztg. **46**, 925, (1922).

mum any such tendency toward polarization. That the primary current distribution is a dimensional function, and is not dependent upon the chemical composition of the solution, is illustrated by the use of a "cell constant" in measuring the conductivity of solutions with alternating current by the customary methods. Even if, as has been found by many, the "cell constant" varies slightly with the composition or concentration of the solution, it is probably because the frequency is not sufficient to eliminate completely the effects of polarization.

The proper spacing of cathodes in a tank, and the use of frames or shields for the purpose of improving the current distribution are purely mechanical arrangements, and bear no direct relation to the properties of the solution.

The primary current distribution as above defined represents the least uniform distribution of current that can be produced in the given apparatus. (In certain cases, if the metal cathode efficiency is lower at low than at high current densities, it is possible for the metal distribution to be less uniform than the primary current distribution.) The actual or "secondary" current distribution in any plating solution is always more nearly uniform than the primary current distribution. The metal distribution ratio is equal to the secondary current distribution ratio multiplied by the ratio of the corresponding cathode efficiencies.

The term "throwing power" as used in electrodeposition has never been clearly defined. In this paper it means "the deviation (in per cent) of the metal distribution ratio from the primary current distribution ratio." In order to define the factors which enter into throwing power, it is convenient to consider the conditions existing upon two parts of a cathode which are at different distances from an anode. It is not necessary to define the actual shape of the anode or cathode, or the distance between them. We may simply assume that the effective resistances from the anode to these two parts of the cathode, respectively, bear a definite ratio to each other, *e. g.*, 1 to 5. On such a cathode, as the current is applied and metal is deposited, the solution adjacent to the cathode tends to become depleted in metal, and an increased potential is necessary for a continuous flow of current. On those parts where the current density is highest, the greatest depletion occurs, hence the potential required to continue deposi-

tion at the high current density would be greater than at the low current density. But as the total potential between the anode and different parts of the cathode is equal, the increase in potential required at the near point is equivalent to an increased resistance at that point. In consequence the current density at the near point is reduced and the current distribution becomes more nearly uniform than the primary distribution.

For practical purposes it is most convenient to consider a concrete example, illustrated in Fig. 1, in which

A = Anode.
C = Cathode.
n = A unit area of the cathode nearest to the anode.
f = A unit area of the cathode furthest from the anode.
R_n = The effective resistance through the solution from the anode to n.
$R_f = KR_n$ = The effective resistance through the solution from the anode to f; where K = Any definite numerical factor, such as 2, 5, etc.
I_n = Current density at n.
I_f = Current density at f.
e_n = Cathode single potential at n.
e_f = Cathode single potential at f.
E_n = Potential drop through solution only, from anode to n.
E_f = Potential drop through solution only, from anode to f.

As the metal of the cathode is always a good conductor (as compared with the electrolyte), we may assume for simplicity that all parts of the cathode are at the same potential with respect to one another; this is equally true for all parts of the anode. During electrolysis between electrodes of the same metal, the total potential difference between a point on the anode and one on the cathode is the sum of three parts, *viz.*, (1) the increase in potential above the static potential at the anode, (2) the potential drop through the solution necessary to overcome the ohmic resistance of the bath, and (3) the increase in potential at the cathode above its static potential.

In practice it is possible to measure directly during the electrolysis,

(a) The potential of the anode against the solution, which as conventionally expressed (*i. e.,* with the sign of the charge on the electrode) has the same sign as the potential to be applied to cause anodic solution. This includes the static potential plus the potential due to polarization.

(b) The potential drop through the solution, which can be conventionally expressed with the sign indicating the direction of flow of a positive current.

(c) The potential of the cathode against the solution, which is equal to the static potential, minus the potential due to polarization.

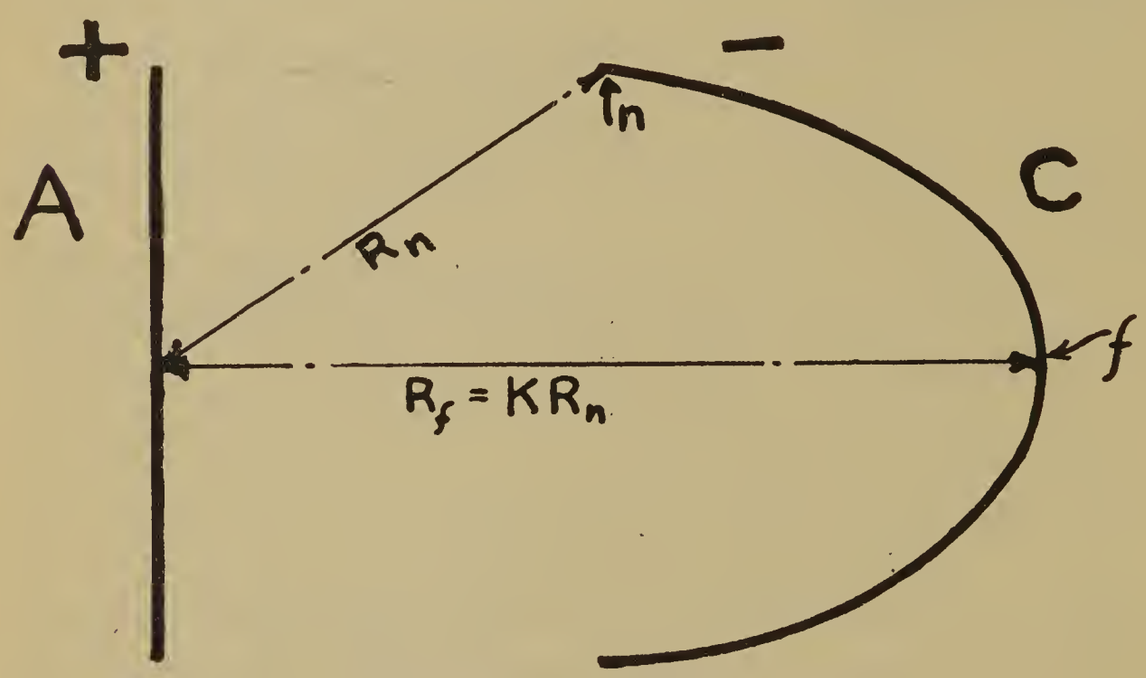


Fig. 1
Illustration of a Simple Case of Throwing Power

As above defined, the sign of the cathode single potential during electrolysis is the reverse of that required for metal deposition; *i. e.,* an equal potential of opposite sign must be applied to cause deposition. The relation of the static, and the dynamic or operating potentials to any zero of reference is illustrated graphically in Fig. 4. As the static potentials of an anode and cathode of similar composition in a given solution must be the same, we may for convenience employ the measured single potentials in the following considerations, instead of deducting from each the static potential in order to obtain the polarization potentials.

The actual potentials between different parts of the anode and the portions of solution adjacent to them are usually not uniform,

and if the behavior or corrosion of an anode were under investigation these potentials at different points on the anode should be measured and considered. For simplicity we may, however, assume that the single potentials on different parts of the anode are or can be made uniform, a condition which has been realized experimentally in the confirmatory tests to be described later. During electrolysis the total potential drops between the anode and the two points on the cathode are equal to each other, *i. e.*,

$$e_a + E_n - e_n = e_a + E_f - e_f \qquad (1)$$

If the anode potential e_a is uniform, it may be eliminated, and therefore

$$E_n - e_n = E_f - e_f \qquad (2)$$

but $$E_n = I_n R_n \qquad (3)$$

and $$E_f = I_f R_f = I_f K R_n \qquad (4)$$

$$I_n R_n - e_n = I_f K R_n - e_f \qquad (5)$$

$$\frac{I_n}{I_f} = K - \frac{e_f - e_n}{I_f R_n} \qquad (6)$$

$$\frac{I_n}{I_f} = K - \frac{e_f - e_n}{\frac{E_f}{K}} \qquad (7)$$

$$\frac{I_n}{I_f} = K\left(1 - \frac{e_f - e_n}{E_f}\right) \qquad (8)$$

$\frac{I_n}{I_f}$ is the ratio of the current densities at "n" and "f," and is therefore a measure of the current distribution. As above defined, K is a measure of the primary current distribution. The actual or "secondary" current distribution $\frac{I_n}{I_f}$ is equal to K minus a correction factor. This correction factor which (together with the cathode efficiencies) determines the "throwing power," involves only those quantities which in experimental work are known or measurable.

Thus far we have considered only the current distribution, which is proportional to the metal distribution, only if at the

respective current densities the cathode efficiencies are both 100 per cent, or at least are equal to each other. In order to compute the metal distribution ratio, it would be necessary to determine the relation between the current density and the cathode efficiency for the particular solutions, and in a given experiment to multiply the observed current densities by the appropriate cathode efficiencies, to obtain what may be designated as the "effective current densities." Then if M_n is the weight of metal upon "n," and M_f on "f," and D_n is the cathode efficiency at "n," and D_f at "f,"

$$\text{The metal ratio } \frac{M_n}{M_f} = \frac{I_n D_n}{I_f D_f} \qquad (9)$$

From this equation it is obvious that, for a given current distribution, the relative metal distribution can be improved by decreasing the current efficiency at the higher current density upon the near point, a condition which is most likely to be realized in cyanide zinc and copper solutions.

A simple numerical method of expressing relative throwing power is essential to any reliable consideration or comparison of the results of different investigators or from different solutions. Any such method must involve some empirical assumption, preferably the so-called primary current distribution ratio, or constant K as above defined. For purposes of record and comparison we would recommend that the throwing power be defined numerically as the *deviation (in per cent) of the metal distribution ratio from the primary current distribution ratio.*

The practical significance of the above definition is involved in the assumption that in commercial plating a certain minimum thickness of metal is required (for appearance or protection) upon the least accessible part of an object, and the aim is to deposit as little metal as possible upon the rest of the object while accomplishing this purpose. A change from 0 to 20 per cent throwing power, as above defined, is equivalent (in a simple ideal case) to the statement that, while depositing the minimum thickness on the far point, 20 per cent less metal will be deposited on the near point than if there were no throwing power.

From equation (8), if the cathode efficiencies at "n" and "f" are equal and T is the throwing power,

$$T = 100 \left(\frac{e_f - e_n}{E_f}\right) \tag{10}$$

If, however, the cathode efficiencies at "n" and "f" are unequal, it may be shown that

$$T = 100 \left[1 - \frac{D_n}{D_f}\left(1 - \frac{e_f - e_n}{E_f}\right)\right] \tag{11}$$

where $\frac{D_n}{D_f}$ is the ratio of the cathode efficiencies at "n" and "f." If this ratio is unity, equation (11) reduces to (10).

The form of equation (10) is of interest, as it shows that with equal cathode efficiencies the percentage throwing power of any solution, in a given apparatus, can be computed from two or at most three potential measurements. The result so obtained is not, however, independent of the value of K, which in any given apparatus will determine the values of the potentials. This equation (10) gives a means of computing the value of K with respect to any two parts of an irregularly shaped cathode under given conditions, if the value of T is computed from the measured potentials, and the ratio $\frac{I_n}{I_f}$ or $\frac{M_n}{M_f}$ is determined by analytical methods.

The practical significance of the above equations may be illustrated by the data from an actual experiment, conducted in the apparatus described later in this paper.

$$K = 5$$
$$e_f - e_n = 0.073 \text{ v}$$
$$E_f = 0.800 \text{ v}$$

according to equation (8)

$$\frac{I_n}{I_f} = K\left(1 - \frac{e_f - e_n}{E_f}\right) = 5\left(1 - \frac{0.073}{0.800}\right) = 4.54$$

If we assume equal cathode efficiencies at "n" and "f,"

$$T = 100\left(\frac{e_f - e_n}{E_f}\right) = 100\left(\frac{0.073}{0.800}\right) = 9.1 \text{ per cent}$$

The ratio $\frac{I_n}{I_f}$ obtained empirically in this experiment was 4.53,

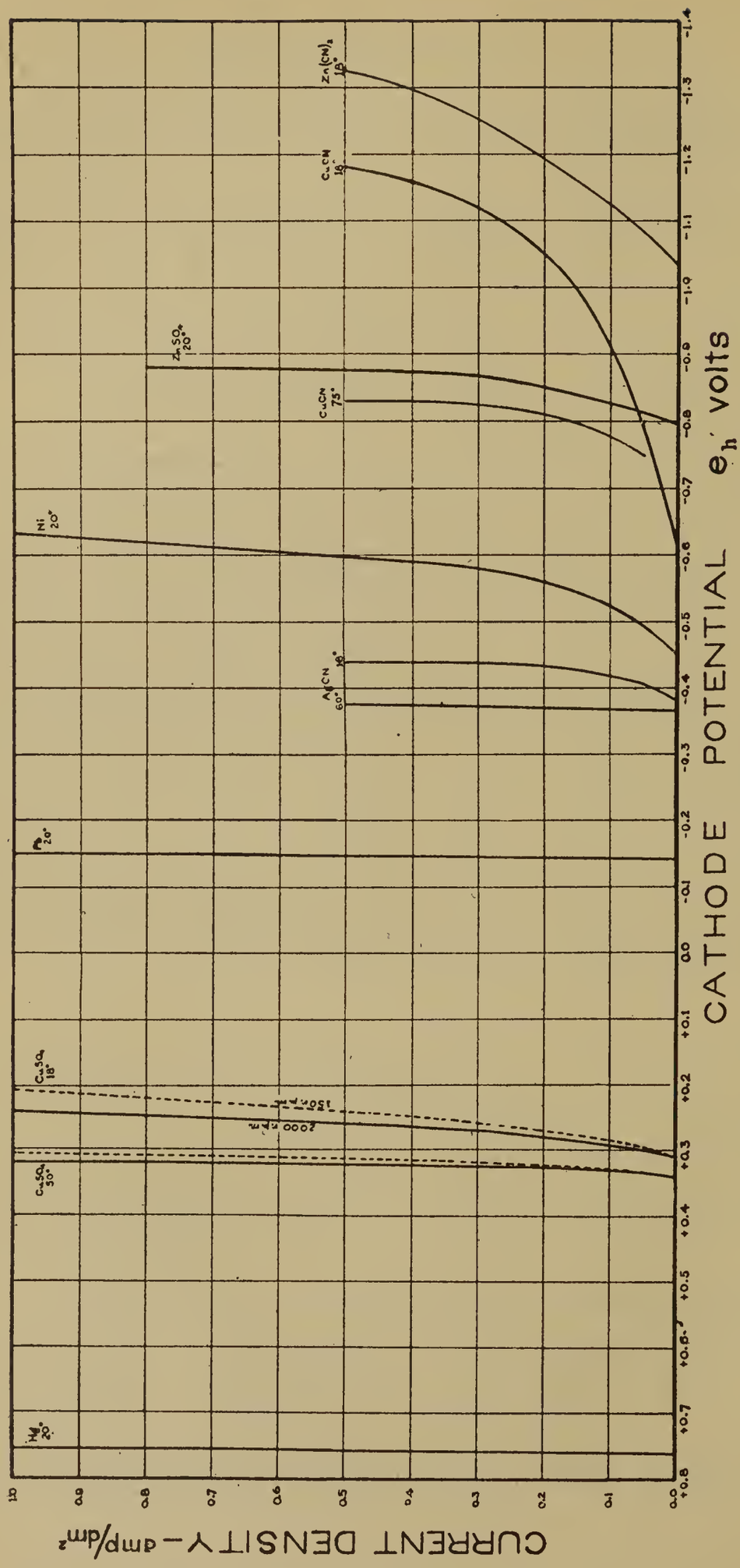


Fig. 2

Current Density-Cathode Potential Curves Derived from Foerster "Elektrochemie Wässeriger Lösungen." 3rd Edition, 1922.

instead of the computed value 4.54. The throwing power calculated from this empirical value was

$$T = 100 \left(\frac{5 - 4.53}{5}\right) = 9.4 \text{ per cent}$$

The effect of the various factors upon the throwing power, may be considered in connection with equation (12) derived from (10).

$$T = 100 \left(\frac{e_f - e_n}{E_f}\right) = 100 \left(\frac{e_f - e_n}{I_f K R_n}\right) = 100 \left(\frac{e_f - e_n}{I_f} \cdot \frac{1}{K R_n}\right) \qquad (12)$$

The determining factors are (1) the difference in the single cathode potentials at the two points concerned *during the passage of a current;* (2) the current density obtained (or desired) upon the least accessible part; (3) the resistivity of the solution (which determines the value of R_n), and (4) the constant K which is fixed by the equipment and arrangement used. The ratio $\frac{e_f - e_n}{I_f}$ is determined by the rate of change of cathode potential with current density over the range employed. If the cathode potentials in any given apparatus and solution are plotted against the corresponding current densities, curves are obtained such as have been published by Foerster and others. Some of those published by Foerster are reproduced in Fig. 2. The value of the ratio $\frac{e_f - e_n}{I_f}$ for given operating conditions is fixed by the slope of the curve between the two current densities, I_n and I_f. The greater the numerical value of this fraction, *i. e.,* the more inclined this portion of the curve is from the vertical, the better will be the throwing power. This is illustrated by a comparison of the curves for copper sulfate and cyanide solutions respectively. The greater slope of the cyanide copper curve is in accordance with the well known superior throwing power of the cyanide solutions.

Another factor which enters into the throwing power is the resistance R_n, or more strictly speaking the solution resistivity R upon which R_n depends. It is obvious that the throwing power of any solution may be increased, either by increasing the value

of the ratio $\frac{e_f - e_n}{I_f}$ or by decreasing the resistivity R, (*i. e.,* increasing the conductivity). Whether any given change in solution composition or operating conditions will increase or decrease throwing power, will depend upon the resultant of the effects upon these two factors. Thus it is entirely conceivable that in any given solution a decrease in resistivity (*e. g.,* by the addition of a "conducting salt") may actually decrease throwing power by reducing the single potential difference proportionately more than it increases the conductivity.

In Fig. 2 the intersections of the curves with the abscissa axis, represent the static single potentials, *i. e.,* the potentials with no current flowing. These static potentials depend upon (a) the positions of the metals in the electrochemical series, and (b) the effective or "thermodynamic" metal ion concentrations in the specific solutions used. The increase in potential at any point on the curve, above the static potential in that solution, may be considered as a measure of polarization, using the latter term in a broad sense.

If we assume as a first approximation, that the single potential of a metal in a given solution is a measure of the effective metal ion concentration in that solution, then it follows that the change in potential during electrolysis is an indication of the reduction in effective metal ion concentration in the film of liquid adjacent to the cathode, which is brought about by the passage of a current. The difference in the throwing power of various plating solutions is then determined by the degrees to which the solution films at any two points on a cathode are depleted in metal ions when different current densities are applied.

The practical significance of the concentration changes at the two points on the cathode lies in the fact that at the point where the primary current density is the highest, the greatest decrease in concentration is produced, the potential to be overcome is increased, and the current density is reduced there to a greater degree than at the least accessible point. Improvement in throwing power by a change in the single potentials, is usually to be sought, therefore, not by making it easier for metal to deposit at the less accessible part, but by making it harder to deposit it at the more accessible point, and thus reducing the current density there.

The improvement produced by increasing the conductivity of the solution is due to the fact that thereby the potential drop through the solution becomes smaller and more nearly equal to the potential difference $e_f - e_n$. The limiting hypothetical case of uniform current distribution is reached when $e_f - e_n$ becomes as nearly equal to E_f as possible, either through an increase of $e_f - e_n$ or a decrease of E_f. This limiting condition is equivalent to a throwing power of 80 per cent if $K = 5$, because when the current ratio $= 1 : 1$, the maximum improvement in ratio is reached; *i. e.*, $100 \times 4/5 = 80$ per cent.

If we assume that all deposition of metal on the cathode takes place by discharge of positively charged metal ions, it is obvious that upon the passage of any current the supply of metal ions, at the cathode will be decreased. In fairly concentrated solutions of a simple highly dissociated salt, *e. g.*, silver nitrate, only a relatively small change in metal ion concentration is thus produced, and the cathode potential necessary for continued deposition is only slightly greater than initially.

If instead, the solution contains a complex salt, *e. g.*, $NaAg(CN)_2$, most of the silver is present in complex anions such as $Ag(CN)_2^-$ and only a small proportion as silver ions, Ag^+. In such a solution it is obvious that (1) the cathode potential necessary to initiate the deposition of silver must be higher than in the $AgNO_3$ solution, and (2) for continuous deposition at a given current density the increase in potential will be greater than in the $AgNO_3$ solution, owing to the much greater *proportional* reduction in silver ion concentration caused by the given current. All solutions with low metal ion concentration will therefore tend to have flat current density-cathode potential curves.

The actual change in cathode potential with current density, *i. e.*, the shape of the curves such as in Fig. 2, is a resultant of a number of factors, among which may be (1) the rate of dissociation of molecules or of complex ions, which may be affected by so-called "reaction resistances," (2) the migration of ions, (3) diffusion of salt molecules, and (4) movement by convection currents.

From the standpoint of throwing power it is immaterial as to which of the above causes contribute to the observed polarization potentials, except in so far as through a knowledge of their relative effects, the polarization can be modified or controlled. It

is probable that differences in the behavior of simple salt solutions are dependent more directly upon convection currents than upon the other three factors. With simple solutions such as the sulfates, it is usually assumed that dissociation and discharge are practically instantaneous. However, with complex ions, such as those present in double cyanides, there is considerable evidence of retarded dissociation or of delayed discharge reactions.

The migration velocities of almost all the ions are of the same order of magnitude, and are all so low that they probably cannot influence greatly the supply of ions at the cathode at any except very low current densities. In those cases in which a large proportion of the metal is in the anions, such as $Ag(CN)_2$, the migration of the metal is toward the anode; which may have a slight effect upon the metal ion concentration at the cathode.

If we assume that the rate of diffusion is determined principally by the osmotic pressure of the solution, all the usual plating solutions must diffuse at approximately the same rate, as they all contain dissociated salts, either of the metal to be deposited or of the alkalis, in about the same concentrations.

The great possible influence of convection currents in determining the effective metal ion concentrations, and hence the cathode potentials, is indicated by the effect of increased agitation upon the shape of the curves for $CuSO_4$ in Fig. 2. From these it may be seen that agitation decreases polarization, and also, as will be shown, it usually decreases throwing power.

It is not necessary however to apply external means in order to produce marked convection currents in the solution. The existence of convection currents during electrolysis has frequently been demonstrated, and it has been shown that at the anode there is usually a downward movement of dense, concentrated solution, and at the cathode an upward movement of light, depleted solution. If then the cathode potential is determined by the composition of the very thin film adjacent to it, the relative effects of convection currents may be great. The principal factors which will determine the rate of such convection upon a given surface, which for simplicity may be assumed to be vertical, are (1) the current density and consequent rate of depletion of the film, (2) the difference in density between the body of the solution and

the depleted film, (3) the viscosity of the solution, and (4) the cathode efficiency and corresponding hydrogen evolution.

For any given conditions the changes in metal concentration caused by a given current density will be similar in corresponding solutions of different metals, as (assuming 100 per cent cathode efficiency) equivalent weights of the metals will be deposited. The change in density produced by a given change in metal concentration may however be very different. This change in any case is proportional to the difference in density between the metal salt solution and the solution formed when the metal is removed. A comparison of various metallic nitrate solutions, Table I, shows the differences in the densities produced by removal of the metal; nitrate solutions are used for illustration, even though not applied in electrodeposition, because a greater number of metals form soluble nitrates. The same conclusions will apply qualitatively whatever metal salts are used.

TABLE I.

Approximate Densities of Normal Nitrate Solutions at 25° C.

Solution	Density	Per cent difference between density of salt solution and HNO_3
HNO_3	1.030	...
$Cu(NO_3)_2$	1.072	4.1
$Ni(NO_3)_2$	1.072	4.1
$Zn(NO_3)_2$	1.073	4.2
$Pb(NO_3)_2$	1.134	10.1
$AgNO_3$	1.135	10.2

From Table I it is apparent that of the metals listed, solutions of three, namely, copper, nickel and zinc, undergo only a small change in density when the metal is removed by electrolysis as compared with the other two, namely, lead and silver. This difference corresponds to the shape of the curves in Fig. 2,[9] in which it is seen that lead fluosilicate solutions produce nearly vertical curves, while those for copper, nickel and zinc sulfates are appreciably inclined especially at low current densities. Note

[9] Apparently all of the curves of Fig. 2 were obtained in agitated solutions. From the shape of these curves it appears probable that the degree of agitation used was not sufficient to obliterate the effects of normal convection currents. If the agitation were sufficient to prevent any depletion at the cathode, all the curves must of necessity be vertical.

also that the curve for mercury deposition is vertical. It seems reasonable to assume therefore that the shape of the curves is determined partly by the changes in solution density caused by the removal of metal.

If hydrogen is evolved at the cathode in any appreciable amount, it will, in rising to the surface, increase the convection currents and will thereby tend to decrease the throwing power.

The effect of the viscosity of the solutions upon the rate of convection is obvious. In general any substance which increases the viscosity will cause the cathode potential-current density curves to become flatter and therefore will tend to increase the throwing power. When very small concentrations of colloids, such as glue, are present in the solutions, their effect upon the viscosity of the solutions as a whole may be negligible. If, however, the glue migrates to the cathode, it seems highly probable that the concentration in the cathode film may become sufficiently great to affect the viscosity. This effect is in harmony with the theory of the "movable diaphragm,"[10] as it is likely that even on minute areas a high concentration of the colloid may hinder the processes of diffusion and convection.

The effect of an elevation in temperature upon the shape of the curves in Fig. 2 is always to make them more nearly vertical. This effect, which is equivalent to an increase in effective metal ion concentration at the cathode, is probably due in part to an increase in the ion migration velocity and rate of diffusion, and to a decrease in the viscosity and in any reaction resistance. When a bath at high temperature is operated in a room at ordinary temperature local temperature differences cause convection currents, which tend to restore the metal ion concentration at the cathode.

IV. EXPERIMENTAL METHODS.

In order to test the validity of the above considerations it is necessary to employ an apparatus in which simultaneously the potentials can be measured and the actual metal distribution can be determined. If then the empirical distribution and throwing power are in accord with those computed from potential measurements, the applicability of the latter is confirmed.

In the few experiments heretofore conducted upon throwing

[10] Englehardt—Trans. Am. Electrochem. Soc. 21, 332 (1912).

power, the distribution of metal was determined upon different parts of an arbitrarily shaped cathode. In one case[11] three small plates were arranged in a plane perpendicular to the anode. In another,[12] one of two metal plates had a circular hole, through which it was necessary for the current to pass to reach the second plate. The principal objections to such devices are (1) the primary ratio is not readily measurable, and (2) the current density on each of the parts compared is not uniform. In consequence any conclusions drawn are purely qualitative. These objections have been overcome in the apparatus illustrated in Fig. 3.

The apparatus consists of a hard rubber box (the joints of which can be made tight with pure rubber cement), the cross section of which, up to the surface of the solution, is 10 x 10 cm. It is 60 cm. long and has in the sides and bottom narrow slots for holding the anode "A" and the cathodes "n" and "f" in any desired positions. As illustrated, the distance from "A" to "n" is 10 cm., and from "A" to "f," 50 cm. *i. e.,* the relative distances are 1 to 5. The anode "A" consists of gauze of the metal to be studied.

The use of gauze was found to fulfil the requirement that the single potential of the anode toward the solution should be practically uniform on both sides. The cathodes are connected by a heavy brass rod B (above the solution). It has been found experimentally by us that in such an arrangement the current densities and cathode potentials are practically uniform over each of the respective cathode surfaces "n" and "f," which therefore represent accurately the two portions "n" and "f" of any cathode such as that shown in Fig. 1. As thus constructed the apparatus is an inexpensive device for measuring under definite and reproducible conditions, the metal distribution upon two plates at the same potential with respect to each other, but situated at different distances from the anode.

The potential measurements were made with normal calomel electrodes and a Leeds and Northrup potentiometer. The tips of the two electrodes were drawn down to narrow capillary tubes less than 1 mm. outside diameter, which were placed in contact with the electrodes, of which the single potentials were to be

[11] Horsch and Fuwa—*Loc. cit.*
[12] Arndt and Clemens—*Loc. cit.*

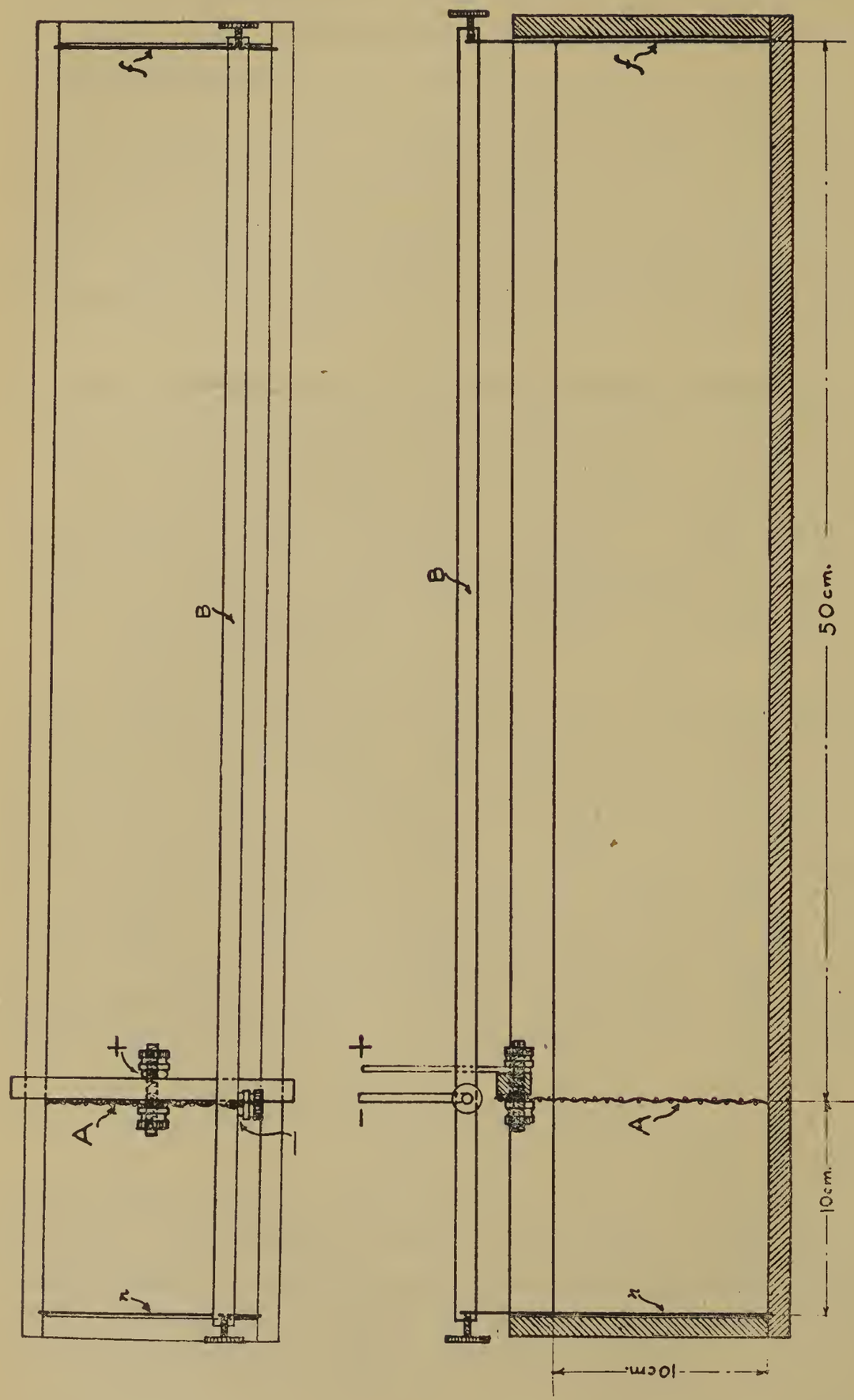


Fig. 3.
Apparatus Used for the Determination of Throwing Power.

measured. By a simple arrangement of the switches, it was possible during electrolysis to measure successively the single potential of "n" and of "f," the difference in their single potentials, the anode single potential, the over-all potential drop between the anode and the composite cathode, and the drop through the solution only, from the anode to each cathode. Not all of these observations were necessary, but they served to check the values required.

TABLE II.

Primary current ratio, 5 : 1 (K = 5). Electrolyte, $CuSO_4$ 1.5 *N.*; H_2SO_4 1.5 *N.* Total current = 2 amp. Time of deposition = 1 hr. Temperature = 21°C. No agitation. Weight of deposit on n = 2.063 g. Weight of deposit on f = 0.456 g.

Single Potentials	Against *N* Calomel Electrode Volts	Against Hydrogen Electrode Volts
e_n	—0.073	+0.210
e_f	±0.000	+0.283
$e_f - e_n$ (computed)	+0.073	+0.073
$e_f - e_n$ (observed)	+0.073	+0.073
e_a (anode)	+0.055	+0.338
Copper static (at n and f)	+0.030	+0.313

Fall in Potential	Volts
E_n	+0.729
E_f	+0.800
E (over all)	+0.856
E computed from A to n	+0.857
E computed from A to f	+0.855

These potentials are illustrated diagrammatically in Fig. 4.

The reasons for devoting our principal attention to the acid copper solution were the wide range of conditions under which satisfactory deposits can be obtained, and the high cathode efficiencies secured. In most cases, therefore, the weights of the metal deposited on "n" and "f" served to measure the currents upon them. When it was necessary to measure the cathode current densities separately, as in nickel deposition or in cyanide copper solutions, the bar B was disconnected, a copper coulometer was

placed in series with each cathode and by means of an adjustable resistance in series with one of the plates the two ("n" and "f") were maintained at the same potential with respect to the anode.

As the formulas derived involve only potential differences the potentials read against the calomel electrode could be employed directly. For purposes of record and comparison however, all values of single potentials have been computed to the hypothetical hydrogen electrode as zero, with reference to which the potential of the N calomel electrode is $+0.283$ v. The signs of the potentials represent the signs of the charge on the metal in contact with the solution. The potential drops through the solution are given signs corresponding to the flow of (positive) current, that is a plus sign represents an e.m.f. in the direction from anode to cathode.

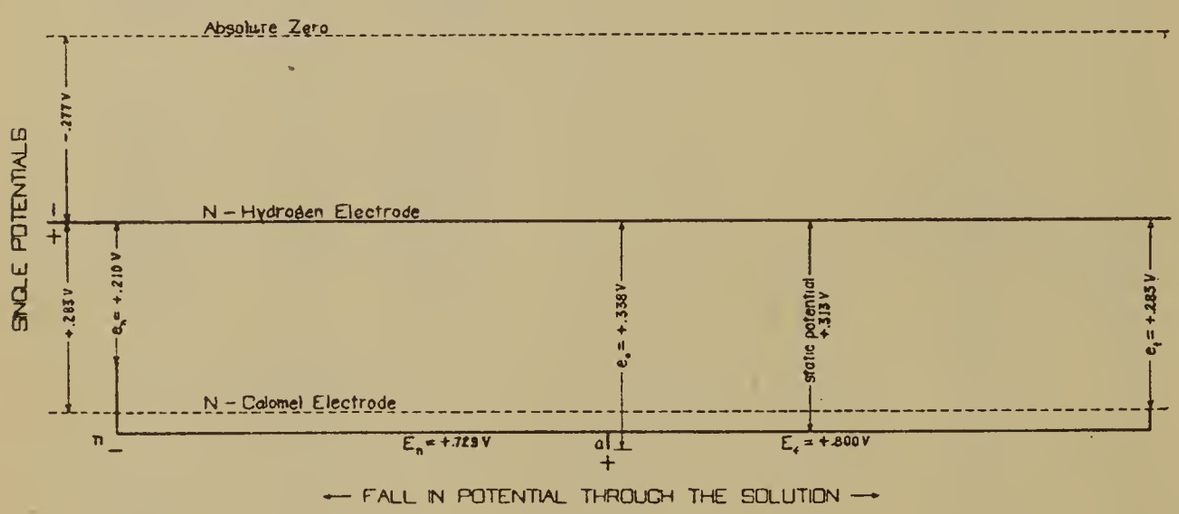


FIG. 4.

Diagram Illustrating the Potential Relations Existing During the "Standard" Copper Sulfate Run.

The method of obtaining and recording the data may be illustrated by a typical experiment recorded in Table II.

No attempt was made to measure these potentials with extreme accuracy. The individual measurements are probably reliable to about ± 0.003 v. No corrections were made for contact potentials, which must be nearly equal in solutions of similar composition, and would therefore be compensated in the potential differences measured or computed. The potentials recorded are those observed after equilibrium conditions were reached, usually in five to ten minutes after electrolysis was commenced. The potentials were usually within about 0.005 v. of their final value in less

than one minute from the beginning of the run. In some experiments the value of $e_f - e_n$ fluctuated by ± 0.005 v. during an experiment. In such cases the average value for the period of electrolysis was employed in the computations. With copper cyanide solutions the same degree of accuracy in potential measurement is more difficult to attain.

In the above experiment the throwing power was computed from the weights of metal on the two cathodes as follows:

$$\frac{2.063}{0.456} = 4.53$$

$$T = 100\left(\frac{5 - 4.53}{5}\right) = 100\left(\frac{0.47}{5}\right) = 9.4 \text{ per cent}$$

Similarly from the potentials

$$\frac{I_n}{I_f} = K\left(1 - \frac{e_f - e_n}{E_f}\right) = 5\left(1 - \frac{0.073}{0.800}\right) = 4.54$$

$$T = 100\left(\frac{e_f - e_n}{E_f}\right) = 100\left(\frac{0.073}{0.800}\right) = 9.1 \text{ per cent}$$

The difference between the current ratio computed from the weights of metal and from the potentials was usually less than 1 per cent of the values concerned. Such agreement is strong evidence of the validity of the equations employed and of the significance of the factors involved.

V. EXPERIMENTAL RESULTS.

(*a*) *Copper Sulfate Solutions.*

The arbitrarily selected set of conditions used in the above illustration were designated as "standard," solely as a basis of comparison, and not as recommended conditions of operation. The current density ratio in the "standard" run was 4.53 : 1, and the throwing power was 9.4 per cent.

The results obtained in acid copper solutions by varying the above conditions are summarized in Tables III to VII, and illustrated in Fig. 5. These results lead to the following conclusions.

1. *Effect of Current Density.* The results shown in Table III and Fig. 5d, indicate that an increase in current density in the so-

called "standard" solution produces little change in throwing power. This behavior is due to the fact that over the range of current densities employed, the curve (Fig. 5d) is nearly a straight line. It is not safe to assume however that the current density is generally without effect upon the throwing power. In all those cases in which the curves become more nearly vertical with increased current density, such as those with dextrin and gelatin, (Fig. 5f, g, h and i), an increase in current density produces a marked decrease in throwing power.

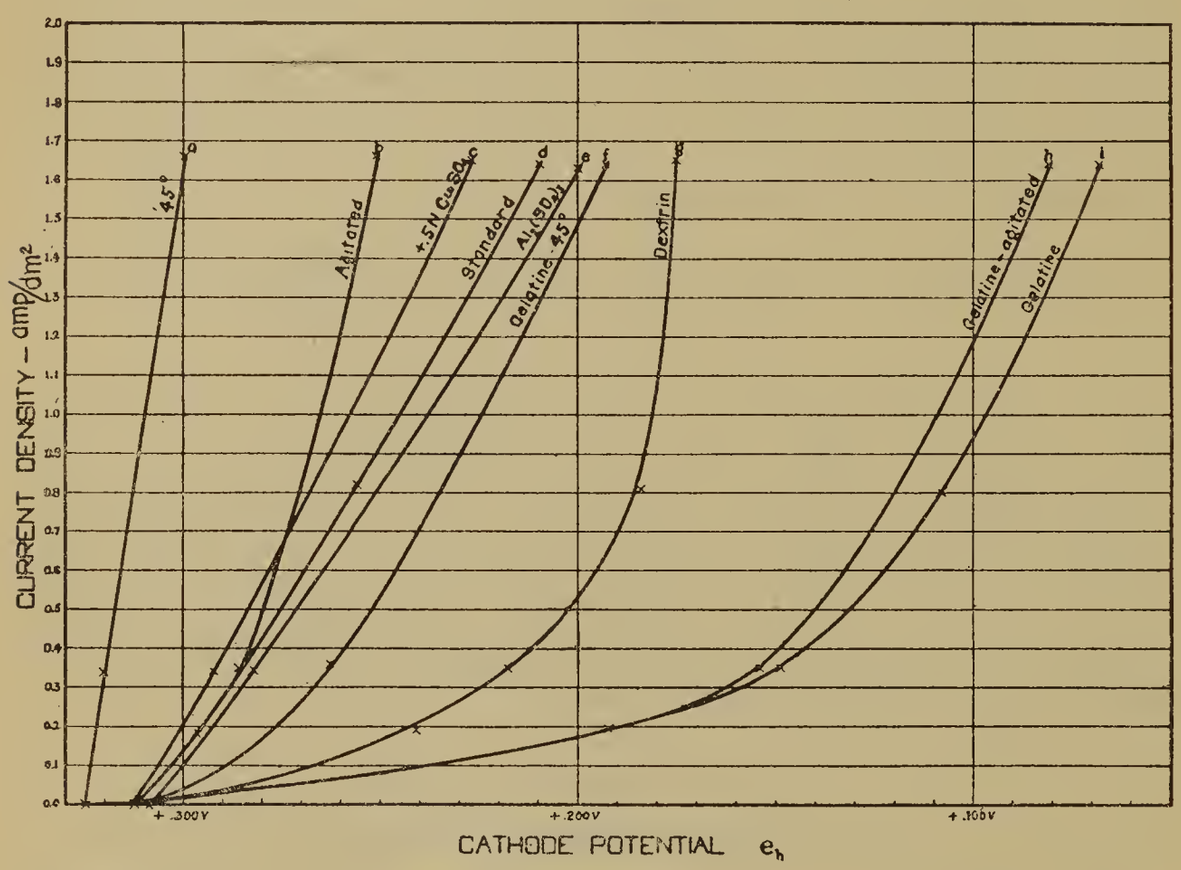


Fig. 5.

Curves Showing the Relation between the Cathode Potential and the Current Density for Various Copper Sulfate Solutions.

2. *Effect of Temperature.* It will be observed from Table IV (and Fig. 5a) that an increase in temperature causes the curve to become more nearly vertical. In consequence the throwing power is decreased, in spite of the fact that the resistivity of the solution is decreased at the higher temperature. Under certain conditions, however, the decrease in resistivity may be the determining factor. Thus in Table VII (Fig. 5i and f) it may be noted that in solutions containing gelatin the slope of the curve,

Table III.

Effect of Current Density

Solution { 1.5 *N* $CuSO_4$ / 1.5 *N* H_2SO_4 } "Standard"

Room Temperature, No Agitation.

Total Current amp.	Time Min.	Metal Ratio		Per Cent. T Obtained	Single Potentials Against *N* H Electrode V.		
		Obtained	Calc.		Static	e_n	e_f
1	60	4.52	4.52	9.6	+0.313	+0.256	+0.295
2*	60	4.53	4.54	9.4	+0.313	+0.210	+0.283
3	40	4.59	4.60	8.2	+0.313	+0.180	+0.277
4	30	4.63	4.62	7.4	+0.313	+0.146	+0.266

Total Current amp.	Time Min.	$e_f - e_n$ v	I_n amp.	I_f amp.	E_f v	R Calc. Ω — cm.	Fig. 5 Curve
1	60	0.039	0.82	0.18	0.409	4.55	d
2*	60	0.073	1.64	0.36	0.800	4.45	d
3	40	0.097	2.46	0.54	1.206	4.47	d
4	30	0.120	3.29	0.71	1.593	4.48	d

* Standard.

Table IV.

Effect of Heat and Agitation.

Solution { 1.5 *N* $CuSO_4$ / 1.5 *N* H_2SO_4 } "Standard"

Total Current—2 amp. Time—1 hr.

Temp. °C.	Agitation	Metal Ratio		Per Cent T Obtained	Single Potentials Against *N* Hydrogen Electrode V.		
		Obtained	Calc.		Static	e_n	e_f
21*	None	4.53	4.54	9.4	+0.313	+0.210	+0.283
45	None	4.89	4.84	2.2	+0.324	+0.299	+0.321
21	Air	4.83	4.81	3.4	+0.313	+0.251	+0.279

Temp. °C.	Agitation	$e_f - e_n$ v	I_n amp.	I_f amp.	E_f v	R Calc. Ω — cm.	Fig. 5 Curve
21*	None	0.073	1.64	0.36	0.800	4.45	d
45	None	0.022	1.66	0.34	0.687	4.04	a
21	Air	0.028	1.66	0.34	0.785	4.62	b

* Standard

in the range from 0.4 to 1.6 amp./sq.dm., is only slightly changed by the elevation in temperature and the throwing power is slightly increased because of the decrease in resistivity.

3. *Effect of Agitation.* In Table IV, it may be observed that agitation produces a marked decrease in throwing power, which corresponds with the curve (Fig. 5, from d to b). A similar though somewhat less pronounced effect is noticeable in Table VII, and Fig. 5, i and h, in solutions containing gelatin. This decrease in throwing power is evidently due to the breaking up of the cathode films and consequent decrease in polarization, especially at the points with high current density.

In certain cases the shape or position of the cathode may be such that there is a tendency for the solution to become "pocketed" and hence depleted in those parts having a low current density. Under such conditions a certain degree of agitation, produced either by mechanical motion of the solution or of the object, may improve the throwing power, provided that the reduction in polarization which it produces at the less accessible point is greater than the change at the more accessible point. It is not safe to assume therefore that agitation is necessarily detrimental to throwing power, although such is usually the case.

4. *Effects of Changes in Content of Copper Sulfate and Sulfuric Acid.* If the content of copper sulfate is increased, the relative polarization produced at a high current density is decreased, and the resistivity is slightly increased, hence the throwing power is diminished, as shown in Table V.

If the acidity is increased, the polarization is changed very slightly, but the resistivity is greatly decreased, because of which latter effect the throwing power is improved, as shown in Table VI. As changes in acidity and copper content have opposite effects, it is possible to secure about the same throwing power with solutions containing these two constituents in quite different proportions.

5. *Effect of Addition Agents.* Many substances have been used or suggested as addition agents in acid copper solutions. It was not feasible to investigate the effects upon throwing power produced by a great variety of such substances, hence a few typical materials were selected, with the results shown in Table VII.

Table V.

Effect of Copper Concentration.

Total Current—2 amp. Time—1 hr.
Room Temperature, No Agitation.

$CuSO_4$ N	H_2SO_4 N	Metal Ratio		Per Cent T Obtained	Single Potentials Against N Hydrogen Electrode V.		
		Obtained	Calc.		Static	e_n	e_f
1.0	1.5	4.46	4.47	10.8	+0.308	+0.201	+0.281
1.5*	1.5	4.53	4.54	9.4	+0.313	+0.210	+0.283
2.0	1.5	4.64	4.63	7.2	+0.313	+0.227	+0.291

$CuSO_4$ N	H_2SO_4 N	$e_f - e_n$ v	I_n amp.	I_f amp.	E_f v	R Calc. Ω — cm.	Fig. 5 Curve
1.0	1.5	0.080	1.63	0.37	0.755	4.08	e
1.5*	1.5	0.073	1.64	0.36	0.800	4.45	d
2.0	1.5	0.064	1.65	0.35	0.877	5.00	c

* Standard.

Table VI.

Effect of Acidity.

Total Current—2 amp. Time—1 hr.
Room Temperature. No Agitation.

$CuSO_4$ N	H_2SO_4 N	Metal Ratio		Per Cent T Obtained	Single Potentials Against N Hydrogen Electrode V.		
		Obtained	Calc.		Static	e_n	e_f
1.5	0.5	4.80	4.81	4.0	+0.311	+0.225	+0.293
1.5	1.0	4.67	4.67	6.6	+0.310	+0.213	+0.285
1.5*	1.5	4.53	4.54	9.4	+0.313	+0.210	+0.283
1.5	2.0	4.46	4.46	10.8	+0.313	+0.214	+0.282

$CuSO_4$ N	H_2SO_4 N	$e_f - e_n$ v	I_n amp.	I_f amp.	E_f v	R Calc. Ω — cm.	Fig. 5 Curve
1.5	0.5	0.068	1.66	0.34	1.755	10.32	c
1.5	1.0	0.072	1.65	0.35	1.096	6.26	d
1.5*	1.5	0.073	1.64	0.36	0.800	4.45	d
1.5	2.0	0.068	1.63	0.37	0.635	3.44	d

* Standard.

(a). *Aluminum Sulfate.* As the presence of aluminum sulfate in copper solutions has often been found to produce smoother deposits, it might be expected also to improve the throwing pow-

TABLE VII.

Effect of Addition Agents.

Solution: 1.5 *N* $CuSO_4$; 1.5 *N* H_2SO_4; + Addition Agent.

Unless otherwise indicated—Total Current, 2 amp. Time, 1 hr. Room Temperature. No Agitation.

Addition Agent	Conc.	Metal Ratio		Per cent T Obtained	Single Potentials Against *N* Hydrogen Electrode V.		
		Obtained	Calc.		Static	e_n	e_f
0	0*	4.53	4.54	9.4	+0.313	+0.210	+0.283
$Al_2(SO_4)_3$	0.5*N*	4.56	4.56	8.8	+0.310	+0.202	+0.282
$Al_2(SO_4)_3$	1.0*N*	4.58	4.57	8.4	+0.310	+0.197	+0.285
$Al_2(SO_4)_3$	1.0*N*†	4.75	4.79	5.0	+0.311	+0.198	+0.283
Dextrose	0.1*M*	4.58	4.56	8.4	+0.310	+0.211	+0.283
Dextrose	0.5*M*	4.65	4.60	7.0	+0.313	+0.206	+0.284
Dextrin	10g./L.	4.72	4.73	5.6	+0.313	+0.175	+0.218
Dextrin	10g./L.‡	4.39	4.37	12.2	+0.313	+0.183	+0.238
Gelatin	0.2g./L.	4.48	4.50	10.4	+0.311	+0.068	+0.148
Gelatin	0.2g./L.‡	4.10	4.07	18.0	+0.311	+0.108	+0.193
Gelatin	0.2g./L.¶	4.45	4.48	11.0	+0.325	+0.193	+0.263
Gelatin	0.2g./L.§	4.51	4.55	9.8	+0.311	+0.080	+0.153

Addition Agent	Conc.	$e_f - e_n$ v	I_n Amp.	I_f Amp.	E_f v	R calc. Ω — cm.	Fig. 5 Curve
0	0*	0.073	1.64	0.36	0.800	4.45	d
$Al_2(SO_4)_3$	0.5*N*	0.080	1.64	0.36	0.902	5.01	..
$Al_2(SO_4)_3$	1.0*N*	0.088	1.64	0.36	1.032	5.73	e
$Al_2(SO_4)_3$	1.0*N*†	0.085	1.65	0.35	2.035	11.62	..
Dextrose	0.1*M*	0.072	1.64	0.36	0.814	4.53	..
Dextrose	0.5*M*	0.078	1.65	0.35	0.963	5.50	d
Dextrin	10g./L.	0.043	1.65	0.35	0.795	4.54	g
Dextrin	10g./L.‡	0.055	0.81	0.19	0.441	4.64	g
Gelatin	0.2g./L.	0.080	1.64	0.36	0.805	4.47	i
Gelatin	0.2g./L.‡	0.085	0.80	0.20	0.455	4.55	i
Gelatin	0.2g./L.¶	0.070	1.64	0.36	0.670	3.72	f
Gelatin	0.2g./L.§	0.073	1.64	0.36	0.807	4.48	h

* Standard. † H_2SO_4 = 0.5 *N*. ‡ Total current = 1 amp. ¶ Temp. = 45° C. § Agitated with air.

er. Actually it was found to have a slightly detrimental effect, which can be accounted for by a small increase in the resistivity of the solution. No marked changes in polarization were ob-

served, such as would occur if appreciable amounts of aluminum hydroxide were formed at the cathode by hydrolysis. In order to make conditions more favorable for such hydrolysis, a run was made with a solution only 0.5 *N* in free sulfuric acid. The throwing power was 5 per cent as compared with 4 per cent obtained in the same solution without aluminum sulfate. These results are of interest as indicating that certain substances may produce an improvement in smoothness without any corresponding effect on throwing power.

(b). *Dextrose.* Frequently commercial glucose and glucose syrup are added to copper plating baths to produce smooth deposits. As these substances are indefinite in composition, it was decided to test separately the effect of the two principal constituents, dextrose and dextrin.

From Table VII it may be noted that pure dextrose, even in fairly high concentration, has only a slight effect upon the throwing power. The small decrease observed is due to the increase in the resistivity of the solution. It was observed that the pure dextrose produces almost no change in the appearance of the deposit.

(c.) *Dextrin.* The first observations made with solutions containing 10 g./L. of dextrin, and with a total current of two amperes, indicated that the throwing power was actually diminished from 9.4 to 5.6 per cent. In view of the fact that preliminary observations with commercial glucose had indicated an improvement in throwing power, it was at first difficult to explain the apparent absence of any effect with either dextrose or dextrin alone. When, however, the experiment with dextrin was repeated at a lower current density, it was found that the throwing power was increased from 5.6 to 12.2 per cent. These facts are illustrated in Fig. 5g, in which it will be observed that at low current densities the curve for solutions containing dextrin is flat, while at higher densities it is more nearly vertical than the "standard" curve. This experience emphasizes the importance of defining all the conditions of operation when the throwing power is specified. In general when irregularly shaped articles are plated, it is necessary to employ a relatively low average current

density, and therefore the shape of the lower portions of the curves is more significant than that of the upper portions.

(d). *Gelatin.* Various forms of glue and gelatin have been frequently used as addition agents in electroplating baths. In the experiments here described a high grade of pure white gelatin was employed. Possibly slightly different numerical results might be obtained with different grades of this material, but the following results are probably typical.

The addition of 0.2 g./L. of gelatin to the "standard" solution when operated under the "standard" conditions, produced a slight increase in throwing power. This effect is due to a slight flattening of the curve in the upper range and not to any appreciable change in the conductivity of the solution. Just as with dextrin it was found that at a lower current density the throwing power was very much increased corresponding to the flat portion of the curve at low current density.

As previously noted, an increase in the temperature of the bath containing gelatine produced a slight increase in throwing power at 2 amp. total current, owing to the fact that the reduction in the resistivity of the solution was relatively greater than the decrease in polarization. Agitation produced a smaller decrease in throwing power than in solutions free from gelatin. This would indicate that the concentration of gelatin in the immediate cathode film may be sufficiently great to increase measurably the viscosity and thus to prevent the displacement of the film by fresh solution.

(*b*). *Copper Cyanide Solutions.*

The experiments with copper cyanide solutions were of special interest because such solutions are known to possess an intrinsically greater throwing power, and also because the cathode efficiencies are usually considerably less than 100 percent. If then the same principles apply to cyanide solutions, it is strong evidence that they will apply to other plating solutions.

The experiments were of the same nature as those with the sulfate solutions but were less extensive. Owing to the greater complexity of the solutions, it was more difficult to secure exact reproducibility. The following arbitrarily selected conditions were designated as "standard," solely as a basis of comparison.

Primary Current Distribution = 5 : 1 (K = 5)

Solution	*N*	g/L.	oz./gal.
CuCN	0.25	22.5	3
NaCN	0.60	30.0	4
Na_2CO_3 (anhyd.)	0.30	15.0	2

At room temperature, about 20° to 23° C. (68° to 73° F.). No agitation. Period of deposition, 1 hr.

The results obtained by varying the above conditions are summarized in Table VIII and illustrated in Fig. 6. These results lead to the conclusions stated on the following pages.

TABLE VIII.

Copper Cyanide Solutions.

Solution { 0.25 *N* CuCN (22.5 g./L.)
0.60 *N* NaCN (30.0 g./L.)
0.30 *N* Na_2CO_3 (15.0 g./L. anhyd.)

No Agitation. Time—1 hr.

Total Current amp.	Temp. °C.	Current Ratio		Efficiency Per Cent		Metal Ratio Obtained	Per cent T Obtained	Single Potentials Against *N* Hydrogen Electrode V.		
		Obtained	Calc.	"n"	"f"			Static	e_n	e_f
0.5*	21	4.18	4.13	61.4	80.2	3.20	36.0	—0.637	—1.547	—1.397
1.0*	21	4.58	4.55	49.1	75.4	2.99	40.2	—0.637	—1.582	—1.442
0.5	45	3.06	3.07	87.3	97.1	2.75	45.0	—0.720	—1.382	—1.097
1.0	45	3.89	3.90	72.4	97.1	2.91	41.8	—0.720	—1.497	—1.237
1.0†	21	4.20	4.19	66.8	90.4	3.10	38.0	—0.592	—1.557	—1.277
0.5‡	21	4.21	4.17	71.4	85.1	3.53	29.4	—0.640	—1.377	—1.237
1.0‡	21	4.68	4.67	...	78.4	...	...	—0.640	—1.397	—1.297

Total Current amp.	Temp. °C.	$e_f - e_n$ v	I_n amp.	I_f amp.	E_f v	R Calc. Ω — cm	Fig. 6 Curves
0.5*	21	0.150	0.403	0.097	0.860	17.7	c,c′
1.0*	21	0.140	0.821	0.179	1.560	17.4	c,c′
0.5	45	0.285	0.377	0.123	0.740	12.0	b,b′
1.0	45	0.260	0.796	0.204	1.180	11.6	b,b′
1.0†	21	0.280	0.807	0.193	1.720	17.8	...
0.5‡	21	0.140	0.404	0.096	0.838	17.5	a,a′
1.0‡	21	0.100	0.824	0.176	1.500	17.1	a,a′

* Standard. † Air agitated. ‡ 2 g./L. $Na_2S_2O_3$ added.

1. *Effect of Current Density.* An increase in current density under "standard" conditions, in both cold and hot solutions, produces relatively little change in the throwing power. Analysis of this rather anomalous situation shows that the *current* distribution is considerably more uniform at the lower current densities but that the *metal* distribution and consequently the throwing power is nearly the same. This fact is due to the marked decrease in efficiency of the cyanide solutions with increased current

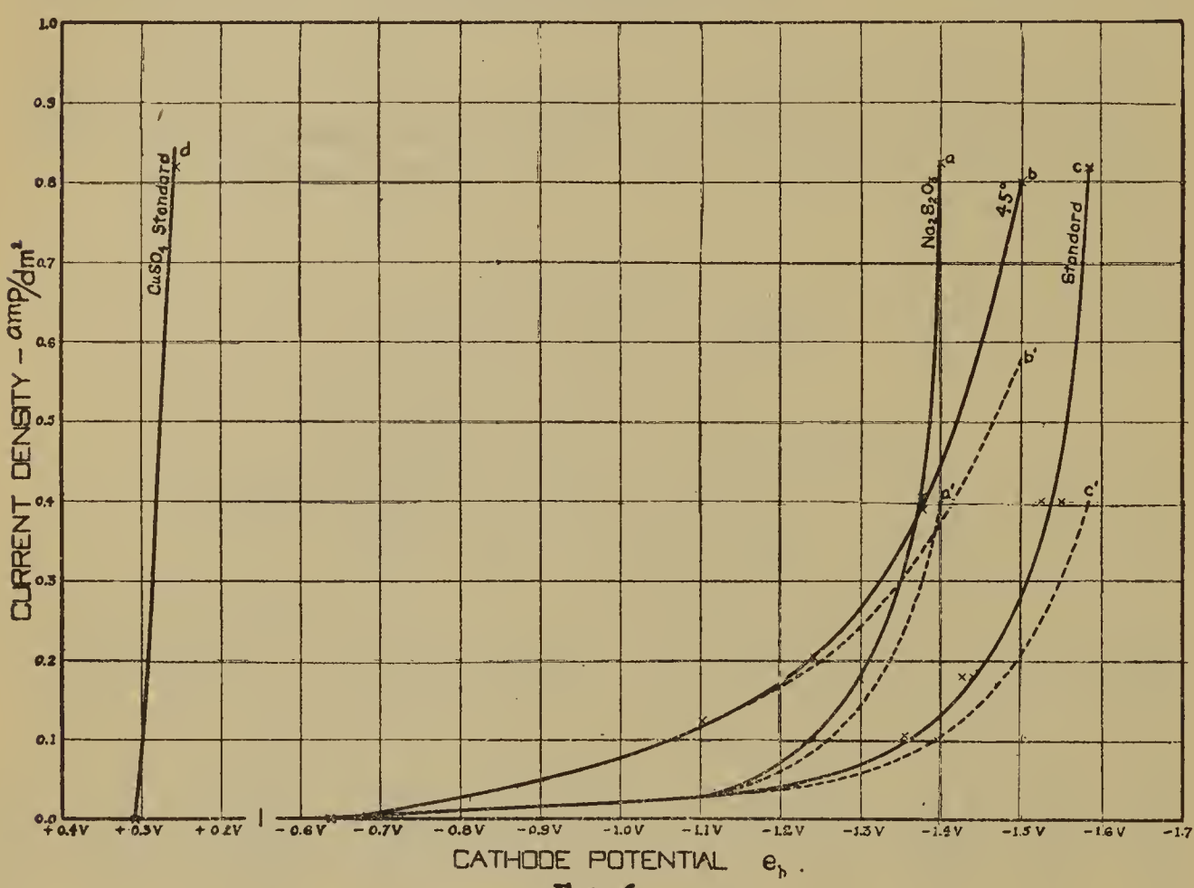


Fig. 6.

Curves Showing the Relation between the Cathode Potential and the Current Density for Various Copper Cyanide Solutions. The dotted lines are the "effective current density"-cathode potential curves.

density. Inspection of Fig. 6 shows that the upper portions of the current density curves b and c are more nearly vertical than are the upper portions of the curves b′ and c′ which represent the "effective current densities."

These experiments are illustrative of the fact that it is possible to secure the same throwing power in either of two ways: (1) by means of good *current* distribution, or (2) by means of a marked decrease in efficiency at the higher current densities. The former procedure naturally tends to produce the better deposit.

2. *Effect of Temperature.* It may be seen that an increase in temperature decreases cathodic polarization (Table VIII, and Fig. 6). Inspection of the curves b and c shows however that the least decrease in cathode potential is effected at the highest current density. This is exceptional. Any factor affecting cathode polarization tends to have its maximum effect where polarization is the greatest, that is at the higher current densities. However, in this case, at the higher current densities the efficiency is quite low as compared with nearly 100 per cent efficiency at the lower current densities. The discharged hydrogen produces considerable agitation of the solution adjacent to the cathode, and as a consequence causes the polarization to be less than it would be if there were no such agitation. Heat, then, has less effect on this already reduced polarization than on the polarization at lower current densities and correspondingly higher efficiencies. Consequently the slope of the current density-cathode potential curve is made flatter with increased temperature. This explains the decided improvement in *current* distribution brought about by heat, at the current densities employed. The resistance of the heated bath is less, and this also contributes to the improvement. The *metal* distribution and the throwing power are only slightly better in the hot than in the cold solution (See curves b′ and c′) This tendency toward equality of the metal distribution ratio is due to the fact that cathode efficiency in the cold cyanide solution is much less than in the hot one.

3. *Effect of Agitation.* Air agitation, although far from an ideal operating condition for cyanide solutions, was employed in a trial run. Under otherwise "standard" conditions it produced an effect not nearly so marked but of the same order as an increase in temperature.

4. *Effect of Sodium Thiosulfate.* Sodium thiosulfate is added to copper cyanide baths because it produces a brighter, smoother deposit. One might predict then that the addition of this salt to the solution would cause the current density-cathode potential curve to be flatter. This, however, is not the case, (see curves c and a, Fig. 6). On the contrary polarization is less when sodium thiosulfate is present, and the curve a is slightly steeper than c. This fact is reflected in the values obtained for the *current* ratios

in the two solutions. Sodium thiosulfate, in the amount used, has no effect on the conductivity of the solution. A comparison of the "effective current density"-cathode potential curves a′ and c′ shows that the metal distribution and throwing power in the two solutions are about the same within the range of the experiments.

VI. PRACTICAL APPLICATIONS.

In all the preceding discussion, an arbitrarily selected primary ratio of 5 to 1 has been adopted for purposes of illustration. No attempt has been made to define the actual current distribution upon any irregularly shaped object, owing to the large number of assumptions that would be involved in such computations. It is believed however that the conclusions regarding the effect of the different variables may be applied qualitatively to most actual plating operations. In the present state of the plating industry, with the difficulty of producing a uniform average current density upon cathodes hung in different parts of a plating tank, there is little reason to predict that the actual distribution or throwing power can be controlled quantitatively.

If in any given operation or experiment, it is known that the effective ratio K has some definite value, such as 10 to 1, it is possible from the data for copper sulfate solutions given in this paper to estimate roughly the throwing power upon such an object under given conditions. This may be done by a series of approximations, in which in each case a definite value of the minimum current density I_f, *e. g.*, 0.1 amp/sq. dm., is employed, as representing a condition desired on the far point. The actual throwing power is that value which when inserted in the equation

$$T = 100 \left(\frac{e_f - e_n}{E_f} \right)$$

corresponds with the values derived from the appropriate curve.

It is not possible to derive any simple relation between the throwing powers with different values of K, as in each case it will depend upon the shape of the corresponding current density-potential curve. A statement of the throwing power in any solution has no significance unless the value of K and of the current density upon at least one of the two parts considered is also specified.

VII. SUMMARY.

1. "Primary current distribution" is that produced when no polarization is involved. It is a dimensional function.

2. "Secondary current distribution" is determined by the composition and electrochemical properties of the solution.

3. "Metal distribution" is determined by the secondary current distribution and the cathode efficiencies.

4. "Throwing power" is defined as the deviation (in per cent) of the metal distribution ratio from the primary current distribution ratio.

5. Throwing power can be computed from the cathode single potentials, the conductivity of the solution, and the current efficiencies. The calculated values agree with those determined empirically.

6. The effect of various factors upon the current distribution and throwing power in copper sulfate and copper cyanide solutions has been determined.

The authors desire to express their appreciation for the suggestions received from George B. Hogaboom and the members of the research committee of the American Electroplaters' Society.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, G. B. Hogaboom in the Chair.

THE ELECTRODEPOSITION OF NICKEL ON ZINC.[1]

By A. Kenneth Graham.[2]

Abstract.

A study of the effect of zinc ions in a nickel plating solution was made and their presence found to be harmful. The advantage of plating zinc with an initially high current density was investigated. A method of determining definite striking conditions is suggested. Finally, the author studied the variation of the electropotential of electrolytic nickel and found that there are other factors besides the effect of hydrogen and oxygen that must be taken into account.

THE EFFECT OF ZINC IN NICKEL PLATING SOLUTIONS.

In connection with a study of the nickel plating of zinc and die castings of high zinc content a number of nickel solutions with various concentrations of zinc were investigated. The fact that solutions for nickeling zinc and die castings, etc., are claimed to work better when old suggested such a study. Zinc would most certainly accumulate in the solution with use. It was thought, therefore, that by adding zinc salts to the nickel electrolyte the extremely high potential of zinc towards the electrolyte could be reduced, thus overcoming some of the difficulties in plating it.

Thompson and Thomas[3] since the completion of this experimental work have studied the effect of zinc as an impurity in nickel plating baths. They used a solution of normal nickel sulfate with ammonium chloride and boric acid, and varied the quantity of zinc from 0.03 per cent to 0.44 per cent (as an

[1] Manuscript received February 2, 1923.

[2] The John Harrison Laboratory of Chemistry, University of Pennsylvania.

[3] Trans. Am. Electrochem. Soc. 42, 79 (1922).

impurity in the nickel salt). A current of 1 amp./sq. dm. (9.3 amp. per sq. ft.) was used. Deposits were made on brass for from 1 to 24 hr.

Hammond,[4] in studying the conditions necessary for the direct deposition of nickel on zinc, found that the usual addition agents to a pickel plating solution did not materially lower the potential of zinc to the solution, but merely changed the permissible rate of deposition. The addition of zinc to the electrolyte was not mentioned.

Schoch and Hirsch,[5] studying the possibility of plating nickel zinc alloys, used electrolytes having a ratio as high as 3 parts of nickel to 4 parts of zinc. They found that the proportion of zinc in the deposit increased with both the concentration and the current density, and that the ratio of zinc to nickel by equivalents in the alloy is from 4.5 to 14 times their ratio in the electrolyte, depending upon the concentration. Above a current density of 2 amp./sq. dm. the ratio of zinc to nickel in the alloy was nearly constant for a fixed concentration.

In the investigations of Schoch and Hirsch and of Thompson and Thomas no attempt was made to plate on zinc. In spite of the above-mentioned behavior of the electrolytes containing zinc, however, and the well-known "black nickeling" tendency[6] of zinc at low values, it was decided to study further the behavior of such solutions in the nickel plating of zinc.

Procedure.

A glass plating jar of 9 L. capacity was used with two rolled sheet nickel anodes each of 90 sq. cm. (14 sq. in.) effective area placed 20 cm. (8 in.) apart. The cathode rod was placed between them 10 cm. (4 in.) from each anode. All cathode plates were cut 7.5 by 8.8 cm. (3 by 3.5 in.) from sheet metal and immersed in the solution to a depth of about 7.5 cm. (3 in.) This gave a plating area of 116 sq. cm. (18 sq. in.) and with the 10 cm. (4 in.) spacing from either anode a fairly uniform current on both sides.

A solution composed of single and double nickel sulfate, with

[4] Trans. Am. Electrochem. Soc., **30**, 103, (1916).

[5] J. Am. Chem. Soc. **29**, 314, (1907).

[6] Nickel solutions containing zinc, and other additions, are used by some to produce a black nickel deposit.

additions of boric acid and magnesium sulfate, was selected from a large number recommended for nickeling of zinc. The composition of this solution was altered from time to time as indicated in Table I.

TABLE I.

Experimental Solutions for Nickel Plating on Zinc.

Solution No.	Nickel Sulfate $NiSO_4 7H_2O$		Nickel Ammonium Sulfate $NiSO_4$ $(NH_4)_2SO_4$ $6H_2O$		Magnesium Sulfate $MgSO_4$ $7H_2O$		Boric Acid		Metallic Zinc as Sulfate		Ratio Metals Zinc to Nickel
	g./L.	*N*	g./L.	*N*	g./L.	*N*	g./L.	*N*	g./L.	*N*	
1	100	0.71	50	0.25	30	0.24	30	0.48	..	...	....
2	100	0.71	50	0.25	30	0.24	30	0.48	1	0.03	1 : 30
3	100	0.71	50	0.25	30	0.24	30	0.48	2	0.06	1 : 15
4	50	0.36	25	0.13	15	0.12	15	0.24	1	0.03	1 : 15
5	50	0.36	25	0.13	15	0.12	15	0.24	20	0.62	4 : 3
6	100	0.71	50	0.25	15	0.12	15	0.24	20	0.62	2 : 3
7	100	0.71	50	0.25	..	...	..	...	..	...	....

It is to be noted that such additions as chlorides, citrates, phosphates, etc., were omitted, although often recommended for plating on zinc. This was done because of the possibility of their altering the effect of the zinc ions. The solution was kept neutral to litmus with ammonium hydroxide.[7]

The plates were thoroughly cleaned with a preparatory cleaner, pumice, cyanide and an electric cleaner before plating. Since the life and quality of any deposit depends so largely on the first film of metal in contact with the cathode, and since this is especially so in the nickeling of zinc where a loose film is likely to be precipitated by immersion, only flash deposits of 3 min. or less were made. These were regarded as sufficient indication of the behavior of the solutions, and served as a satisfactory means of comparison.

Results.

In plating on zinc from a single and double nickel sulfate solution (No. 7) it was found that good flash nickel deposits could be obtained at densities varying from 3.0 to 6.0 amp./sq. dm. (27

[7] The hydrogen ion concentration was not measured. Considering the nature of the results this omission is not so serious. Had affirmative results been obtained the hydrogen ion concentration would most certainly have been investigated.

to 54 amp./sq. ft.) by a proper regulation of the time. It was also found that the presence of magnesium sulfate and boric acid did not apparently affect the deposition, but that the presence of zinc was a decided disadvantage.

This is an apparent contradiction of the practical platers' claim that a solution that has been used for nickeling zinc, die castings, etc., works better when old. This would seem to indicate that the accumulation of zinc ions in the solution with time, as would certainly be the case, is not objectionable. As a result of our study, however, it is felt that the presence of zinc in any concentration is undesirable, and that the possible advantages to be found in the use of an old solution cannot be attributed to the zinc ions that it may contain.

THE DIRECT NICKELING OF ZINC.

In the direct nickeling of zinc the desirability of plating at an initially high current density is quite widely recognized, but to accomplish this in practice in a plating tank partly filled with work is so difficult that it is frequently neglected, with resulting difficulties that are unfortunately too common. The use of a separate solution, permitting higher current densities and definite striking conditions, involves an additional operation, but in spite of this the advantages of this practice are so marked that it was decided to investigate further its possibilities.

When plating any metal (zinc) of high solution pressure with a metal (nickel) possessing a lower solution pressure there are two reactions to be considered. The first is the precipitation by immersion, and the second is the electrodeposition of the ions of the metal possessing the lower solution pressure on the more negative cathode metal, zinc. To obtain a good adherent deposit, therefore, one must either lower the potential of this cathode metal, *e. g.*, by some addition agent, or so determine the conditions of plating that the rate of the first reaction is not only reduced to a minimum, but greatly exceeded by the rate of the second reaction, *i. e.*, the depositing of nickel.

Hammond[8] in his study of the electrodeposition of nickel states that zinc requires a higher current density, especially at the beginning of the electrolysis, to coat the metal quickly with nickel so

[8] Trans. Am. Electrochem. Soc. **30**, 103 (1916).

as to minimize deposition by immersion. The chlorides and citrates as used in his solution did not materially alter the potential of zinc to the solution and were, therefore, only of value in so far as they increased the permissible rate of deposition.

Hammond's Solution.

	g/L.	*N*
$NiSO_4.7H_2O$	240	1.71
$NiCl_2.6H_2O$	10	0.08
H_3BO_3	30	0.48
Sodium citrate	175	...

It appears, therefore, that little can be accomplished toward lowering the potential of zinc, and that success in plating it depends almost entirely on the initial rate of deposition. To first strike the zinc before plating, in a solution kept just for that purpose, would not only prevent the accumulation of zinc in the regular plating solution, but would permit the use of higher densities than are possible in the regular solution, both of which are desirable.

Procedure.

A solution of the following composition was used in this investigation,

$NiSO_4.7H_2O$	108 g./L.	0.712 *N*.
$NiSO_4.(NH_4)_2SO_4.6H_2O$	50 g./L.	0.254 *N*.

As the rate of deposition by immersion increases with the concentration, the nickel content was made considerably lower than that recommended above by Hammond. The other constituents recommended by him were omitted since the anode corrosion was not of great importance in this work and it greatly simplified the control of the solution.

A glass plating jar of 9 L. capacity was used with two rolled nickel anodes, each with an area of 90 sq. cm. (14 sq. in.). The cathode rod was placed between them 10 cm. (4 in.) from each anode. The cathode plates were cut 7.5 cm. (3 in.) wide and about 10 cm. (4 in.) long. After cleaning, the upper end was dipped in melted wax as a stopping off material, so that the

cathodic plating area was exactly 7.5 by 7.5 cm. (3 by 3 in.). This gave a plating area of 116 sq. cm. (18 sq. in.) and with the 10 cm. (4 in.) spacing from either anode a fairly uniform current on both sides.

As a means of determining when sufficient nickel had been deposited on the cathode by striking to permit its being plated under the usual conditions without the danger of secondary reactions, the following was suggested: To measure the single electrode potential[9] of the cathode as the nickel was deposited until it had reached such a value as experiment should prove to be free from the above reactions.

TABLE II.

Conditions Observed While Plating on Zinc.

Electrode potential volts	Current density amp/sq. dm.
—0.473	0.00
—0.460	0.85
—0.555	1.75
—0.573	2.63
—0.655	3.50
—0.680	5.00
—0.173	0.00

Accordingly, a calomel electrode was prepared, using normal potassium chloride, of which the potential is +0.560 volt at 18° C., with reference to the absolute zero of potential. This was employed as a comparison electrode according to the method suggested by Sand[10] with the one exception that a Leeds and Northrup sensitive galvanometer was used instead of an electrometer. It was soon found that at the high current densities used in striking, the potentials observed were largely influenced by the hydrogen evolution and surface reactions as Table II would indicate.

This phenomenon has already been observed in the case of

[9] The potential which the metal assumes with respect to the solution in which it is placed. For zinc it is negative.

[10] J. Chem. Soc. 91, 374 (1907).

nickel[11] and iron[12] salts, which Foerster believes to be due to the slow rates at which the reactions $Fe^{++} \rightarrow Fe + 2 \oplus$ and $Ni^{++} \rightarrow Ni + 2 \oplus$ proceed. It was necessary, therefore, to interrupt the current to allow the surface film of electrolyte to reach an equilibrium before making such observations. The values recorded below are therefore static potentials, measured with the current off, unless otherwise stated.

It is significant that all potential observations were made in a separate solution of constant composition at approximately the center of the cathode. The center of the cathode received less current than the edges, and consequently less metal, with the result that it took a longer time to cover. This was then the logical place to measure the potential, as it was the most difficult to plate.

Results.

The electro-potential of zinc to the solution in Run 1 was —0.473 volt. While it was found possible to obtain good nickel deposits by striking at lower densities for longer periods of time than in this run, yet these potentials are only slightly lower than zinc itself. This is because it was necessary to let the plate hang in the electrolyte with the current off during the potential measurements, and at places where the deposit was thin or the zinc was still exposed a secondary reaction in the nature of a cell effect rapidly destroyed the nickel deposit.

The plates used in Run 2 were weighed after a preliminary cleaning. They were then given a light electric clean and a cyanide dip before plating. After plating they were washed, dried and weighed. The difference was taken as a fairly accurate value of the weight of nickel deposited. The potential measurements had to be made on other plates run under analogous conditions, because where secondary reactions occurred the deposits were destroyed. Plates numbers 35, 36 and 37 showed no signs of these reactions.

The variation of both the time and the potential with the weight of metal deposited is better illustrated by the curves of

[11] Schweitzer, Z. Elektrochemie, 16, 602 (1909).
[12] Foerster and Mustad, Abhand. Bunsen Ges. 2, 44 (1909).

TABLE III.—*Data of Run 1.*

Plate No.	Time sec.	Current amp/sq. dm.	Cathodic Potential volts
46	15	4.0	—0.473
45	30	4.0	—0.470
44	45	4.0	—0.470
43	60	4.0	—0.465
42	120	4.0	—0.430

TABLE IV.—*Data of Run 2.*

Plate No.	Time sec.	Density amp./ sq. dm.	Nickel gm./ sq. dm.	Cathodic No.	Potential volts	Volts	Remarks
12	15	5.0	0.0201	..	—0.466	6.5	Center exposed
13	30	5.0	0.0390	..	—0.406	6.5	Center exposed
16	45	5.0	0.0682	..	—0.306	6.5	Center exposed
17	60	5.0	0.0833	..	—0.270	6.5	Nearly covered
18	75	5.0	0.1070	35	—0.250	6.5	Covered
19	90	5.0	0.1306	36	—0.230	6.5	Covered
14	105	5.0	0.1519	37	—0.210	6.5	Covered

TABLE V.—*Data of Run 3.*

Plate No.	Time sec.	Density amp/sq. dm.	Cathodic Potential volts	Remarks
52	15	6.0	—0.455	Center exposed
51	30	6.0	—0.300	Center exposed
50	45	6.0	—0.273	Nearly covered
49	60	6.0	—0.265	Covered
48	120	6.0	—0.173	Covered

TABLE VI.—*Comparison of Runs.*

Run No.	1	2	3
Density amp/sq. dm.	4.0	5.0	6.0
Time sec.	Potential volts	Potential volts	Potential volts
15	—0.473	—0.466	—0.455
30	—0.470	—0.406	—0.300
45	—0.470	—0.306	—0.273
60	—0.465	—0.270	—0.265
120	—0.430	—0.188*	—0.173

* Value taken from curve, Fig. 2.

Fig. 1. It is possible from such curves to determine the weight of metal necessary to produce a given potential or even the time required. As a method of determining the proper time of striking, and as a means of determining the weight of metal required to resist at least the temporary action of an electrolyte, this may be recommended.

In Run 3 at 45 sec. sufficient metal was deposited so that very little secondary reaction was in evidence while making the poten-

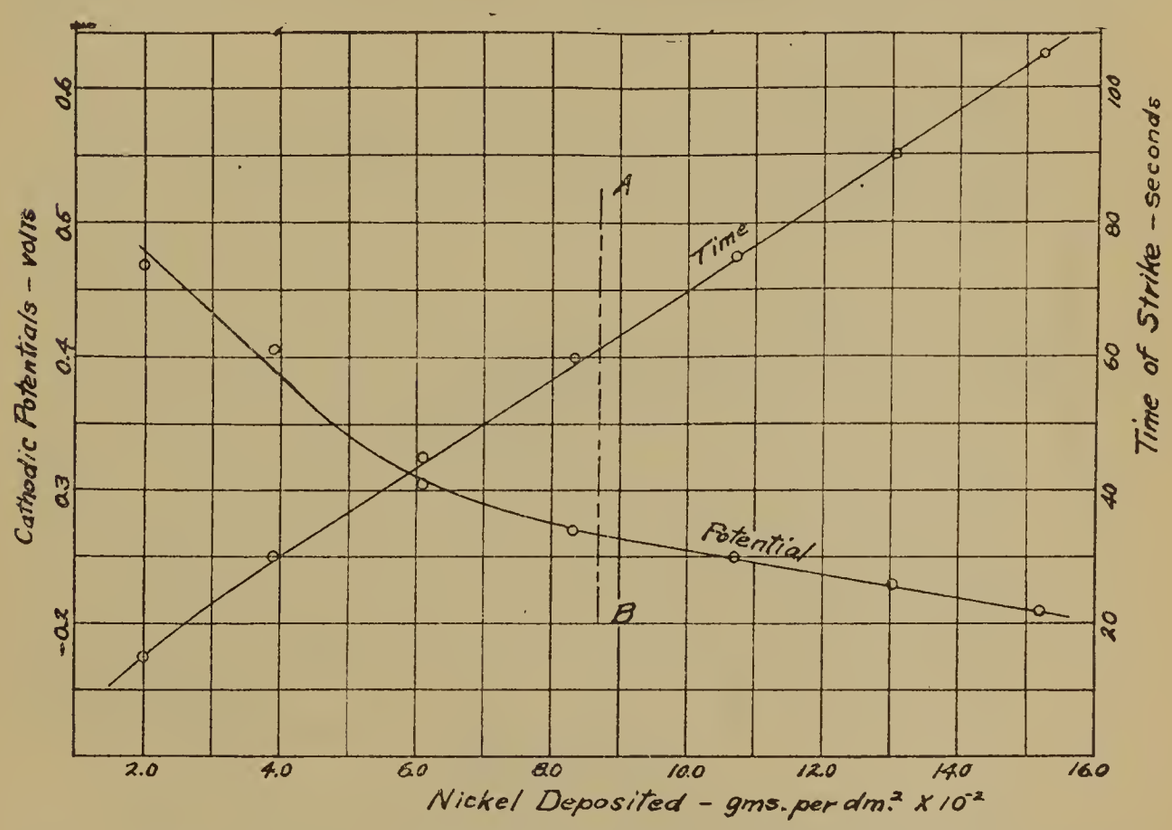


FIG. 1. Curves of Cathodic Potential and Time vs. Nickel Deposited. Current Density—5 amp./sq. dm.

tial measurement. At 60 sec. and over the plate was completely covered and showed no reaction. At any potential above —0.265, therefore, the danger point is passed and the plating can be continued under ordinary conditions.

The results recorded in Tables III to VI are clearly represented by the curves of Fig. 2. After the potential had reached a value on the flat portion of the curve which corresponds to a potential of —0.265 volt or higher (more positive) the behavior is regular. These values are below the line AB.

VARIATIONS OF THE ELECTROPOTENTIAL OF ELECTROLYTIC NICKEL.

After measuring the change of potential of sheet zinc as the time of plating and the weight of nickel deposited increased, it was decided to continue the plating long enough to have an all nickel surface, and to observe the resulting potential of the electrolytic nickel and the time required to produce it. It was not possible to get reproducible results, however, and further experimenting only substantiated the observations of others, and confirmed the generally recognized fact that there are many variables which can influence the equilibrium potential of nickel. The

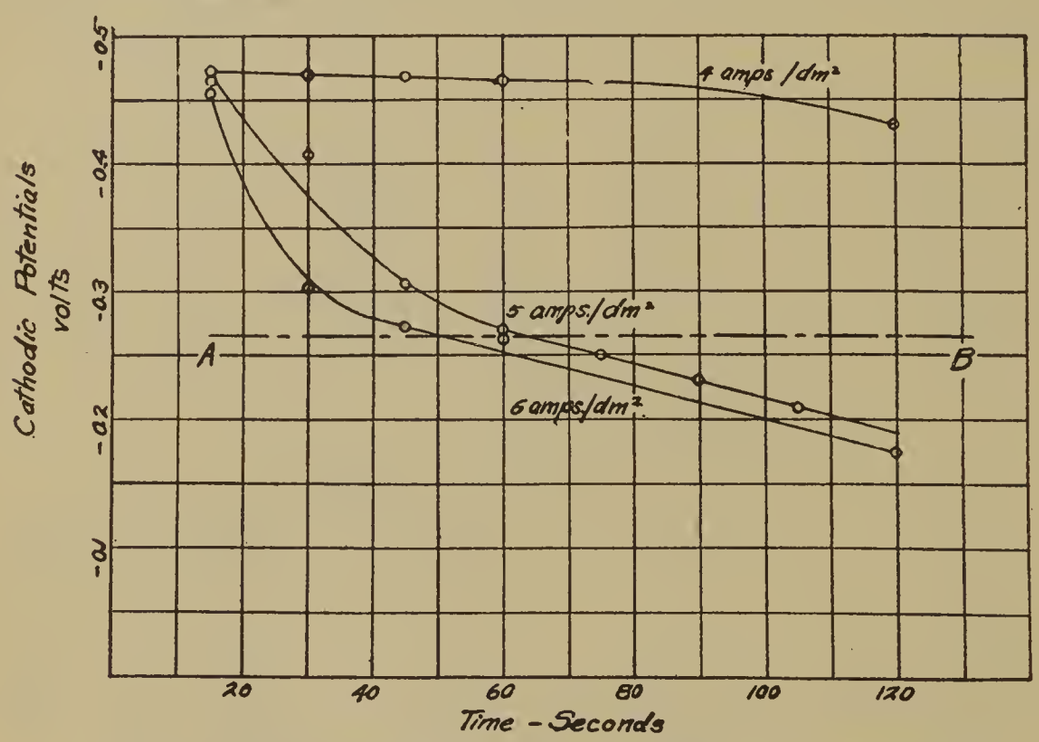


FIG. 2. Curves of Potential vs. Time for Different Current Densities.

numerous irregularities mentioned in the literature not only verify this, but emphasize the need of a better understanding of the factors involved.

After a rather extensive study of the subject as it is found in the literature the writer must admit that there is very little definite knowledge to be had. The most comprehensive treatment is to be found in the experimental part of Smits'[13] book on "The Theory of Allotropy" where mention is made of some results of as yet unpublished investigations on nickel and cobalt.

"When an inert metal is placed in a solution from which, theoretically, it should liberate hydrogen, a disturbance of the metal

[13] Theory of Allotropy, pp. 321-329.

in the direction of greater nobility occurs, which in particular cases may proceed until the hydrogen potential is reached."

This was verified experimentally with both nickel and cobalt. He concludes, therefore, that not only oxygen, but hydrogen also, is capable of disturbing the equilibrium potential of such metals. He then adds that "It is clear that the only certain method of determining the equilibrium potential of inert metals in general, and of nickel in particular, is to carry out the measurement in solutions which are as free as possible from both oxygen and hydrogen."

It is evident, therefore, that the above application of electropotential measurements as attempted by the writer is not practical, because of the necessary refinements in their determination, and the wide variation in the values obtained when these precautions are not observed.

Of the various factors affecting the equilibrium potential of nickel, therefore, hydrogen and oxygen have been mentioned. Smits suggests the possibility of allotropy, on which basis he explains the results of various investigators, and in cases where a wide range of current density is employed in preparing electrolytic deposits, as in some of the writer's experiments, the difference in crystal structure of the deposit and the appearance of passive phenomenon may be contributing causes of the irregularity observed.

CONCLUSION.

The zinc is covered so rapidly at the higher densities that not only is the possibility of secondary reactions reduced to a minimum while plating, but within 75 sec. at 5 amp./sq. dm. and 60 sec. at 6 amp/sq. dm. the potential had become positive enough (—0.265 v. to the solution used as compared to —0.473 v. for sheet zinc) to eliminate entirely the danger. If in plating zinc, therefore, the article is first plated in a striking solution at a high density, until the potential at the most difficult point to cover is equal to or above (more positive) this determined critical value, and then transferred to the regular nickel solution to be plated under the usual conditions, it is believed that little further difficulty will be experienced.

In general, as a method of determining the proper striking con-

ditions in the plating of any metal, that employed in the case of run No. 2, in which the effect of variations in time and potential vs. weight of deposit are directly determined, seems worthy of possibilities.

The writer wishes to thank Dr. H. S. Lukens for his many suggestions and kind supervision of this investigation.

DISCUSSION.

C. P. MADSEN[1]: What was the degree of adherence obtained in those deposits, particularly by sharp bending?

A. K. GRAHAM: We did bend some of our specimens and they adhered readily.

[1] Consulting Engineer, New York.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, G. B. Hogaboom in the Chair.

THE EFFECT OF IRON ON THE ELECTRODEPOSITION OF NICKEL.[1]

By M. R. Thompson.[2]

Abstract.

A number of previous investigations are reviewed, and it is concluded that the results may have been influenced by lack of regulation of the hydrogen ion concentration or pH. It is shown that, if the pH is properly controlled, the presence of iron in nickel solutions does not necessarily cause cracking or peeling of the deposits, as it has often been supposed to do. Deposited iron has a primary effect upon the crystalline structure of nickel deposits, rendering the latter finer-grained and therefore probably harder, although more brittle. Occluded basic precipitates containing iron may injure a deposit by making it porous, or dark in color.

CONTENTS.

I. General.

II. Discussion of the work of other investigators. Adams; Foerster; Calhane and Gammage; Bennett, Kenny and Dugliss; Bennett, Rose and Tinkler; Mathers and Sturdevant; Mathers, Stuart and Sturdevant; Küster; Toepffer; Kohlschütter and Vuilleumier; Schlotter; conclusions.

III. Experimental work. The pH of iron solutions; preliminary electrolyses; electrolyses at constant pH; appearance of deposits; structure of deposits; colloids; amount of iron in plating baths; amount of iron in deposits; occlusion of iron.

IV. Conclusions.

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Manuscript received February 5, 1923.

[2] Chemist, Bureau of Standards, Washington, D. C.

I. GENERAL.

In the electrodeposition of nickel, iron is almost always present, being found in anodes, solutions and deposits. Its presence is usually taken for granted, and its effect upon the operation is but little considered or even known, at least in this country. The amount of critical discussion upon its effect that has appeared within recent years has been very limited, and largely influenced by certain experiments and conclusions discussed by Foerster many years ago. In fact there has been little more than repetition of those conclusions, which will be considered later in this paper.

Some recent studies by the author have led to conclusions somewhat at variance with those found in the literature. In these experiments, hydrogen ion concentration was taken into account by means of methods lately adopted by the writer[3] and others for this purpose. It is hoped that the presentation of our results at this time will be helpful to other investigators of the important general subject of nickel deposition, by aiding in the settlement of a somewhat obscure detail of this field.

II. DISCUSSION OF THE WORK OF OTHER INVESTIGATORS.

In an early paper upon nickel plating, Isaac Adams[4] stated: "The iron dissolves with the nickel as ferrous sulfate; a certain portion of it is oxidized by the air and goes over into ferric sulfate, is hydrolyzed, and precipitates as ferric hydroxide; but I am certain, from experiments that we have made, that some of the iron remains in solution as ferrous sulfate. From a solution containing ferrous sulfate and nickel sulfate, at least the same percentage of iron is precipitated (deposited) as occurs in the solution; consequently, the conclusion that I draw (and I hope we may get some information from people that know more about it than I do) is, that all our nickel plate contains iron."

Adams referred to work with anodes containing from 6 to 10 per cent of iron. In the discussion of his paper there was some comment made on the possible effect of deposited iron upon the rusting of nickel plate, also on the probable necessity of iron

[3] The Acidity of Nickel Depositing Solutions. Trans. Am. Electrochem. Soc., **41**, 333 (1922).

[4] Isaac Adams. The Development of the Nickel Plating Industry, Trans. Am. Electrochem. Soc., **9**, 217 (1906).

in the anodes to make the latter dissolve readily in solutions not containing chlorides, and the advantage of using instead pure nickel anodes in a chloride bath and thus eliminating iron from the system.

Foerster[5] has summarized some of the early data upon the effect of iron: "The phenomena are further complicated by a time effect upon the composition of the alloys deposited at the cathode if the metals iron and nickel, both distinguished by high polarization, are present in the solution. Although nickel in pure form is considerably easier to deposit than is iron, a nickel-iron alloy separates containing a good deal higher proportion of iron than exists in the solution,[6] *e. g.,* if in a solution which contains one gram equivalent per liter of total metal as sulfate, the iron amounts to 2, 10, 50 or 75 per cent of the total metal present, the deposit will contain 13, 22, 72 or 89 per cent of iron, at 50° C., current density of 1.25 amp./sq. dm. and an acidity of 0.03 N H_2SO_4.[7] By continued electrolysis of an electrolyte with composition held constant, the iron content of the alloy decreases, rapidly at first, then slowly, finally becoming constant, *e. g.,* from a solution containing 1 gram equivalent of total metal per liter and 2 per cent of it iron, at 20° C., current density of 1.25 amp./sq. dm., acidity of 0.03 N H_2SO_4, the first 0.04 g. of alloy upon 1 sq. dm. contained 24.6 per cent Fe, while in the layer from 0.4 to 0.7 g. the iron content was only 12.2 per cent. Because the iron content affects the mechanical properties of the alloy, the varying composition of successive layers produces stresses, which bend the cathode edges toward the anode, or else the deposit breaks away from the base in pieces and rolls up into half-cylinders or scales, which are open toward the anode; *the metal exfoliates from the cathode.* With increasing temperature, the proportion of iron to nickel in the alloy becomes closer to that existing in the solution, and its variability constantly decreases as the thickness increases and thereby the tendency toward exfoliation. The reasons for the variations in the com-

[5] F. Foerster, Elektrochemie Wässeriger Lösungen, 3rd ed., 376 (1922).

[6] F. Foerster, Z. Elektrochem. 4, 162 (1897); C. Engemann, Dissert, Dresden, 1911; Z. Elektrochem. 17, 910 (1911); R. Kremann, C. Th. Suchy u. R. Maas. Sitsungsber. der Wiener Akad. d. Wissensch. 122, 999 (1913) and Monatshefte f. Chemie (Vienna) 34, 1757 (1913).

[7] The probable pH would be between 1 and 2. (M. R. T.)

position of the alloy layers deposited under constant external conditions, especially the prevailing cathode potentials, have not yet been discovered."

Elsewhere, Foerster[8] states: "Good deposits thicker than 0.01 mm. can seldom be secured from solutions even of low iron content without a tendency toward exfoliation being noted, while if solutions are entirely free of iron, smooth and solid deposits of 0.1 mm. or greater thickness can be made, at 20° C., current density 2.5 amp./sq. dm., solution *N* in $NiSO_4$."

Also, "In general, the cause of exfoliation being certainly known, the industry should devote more attention than formerly to the convenient removal of iron from the nickel bath."

He proceeds to offer a possible explanation for the improvement in deposit sometimes claimed to take place after a freshly-prepared bath has been electrolyzed for a time. Iron in nickel solutions tends to deposit more readily than nickel, consequently the amount of iron in solution at the start gradually decreases to a minimum maintained by iron from the anodes. The earlier deposits would be higher in iron content, and therefore probably poorer than the later ones.

This explanation is based upon a greater proportion of iron in the salts used to prepare the bath than in the anodes. At the present time, in this country, such a condition is probably uncommon, and, in fact, samples of commercial salts are sometimes quite free of iron,[9] while even the high grade 95-97 per cent anodes always contain some iron. From the plater's standpoint, therefore, the explanation of the "breaking-in" or "working-out" of a new bath probably lies elsewhere and it would seem unwise to generalize upon the subject.

In view of the supposed serious effect of iron upon the deposited nickel it is difficult to see how some of the experiments referred to above, in which good deposits very high in iron were obtained, could have been satisfactorily conducted. Similar considerations apply to experiments of Toepffer, yet to be considered. In cases where a tendency to peel was observed by Foerster the

[8] Foerster, 3rd Ed., 1922, 491.

[9] M. R. Thompson and C. T. Thomas, The Effect of Impurities in Nickel Salts Used for Electrodeposition. Trans. Am. Electrochem. Soc. 42, 79 (1922).

deposits were probably always rather thin, but in some of those by Toepffer, relatively thick deposits were made.

Calhane and Gammage[10] investigated this subject. In their work the anodes used contained 92 per cent Ni and 7.5 to 8 per cent Fe, and two anodes and one cathode were used per cell. The volume of electrolyte per cell was 3 L. and the composition was nickel-ammonium sulfate 0.42 *N*; (83 g./L. or 11 oz./gal.) The time of deposition varied from 1 to 3 hours. The cathode current density varied from 0.2 to 4 amp./sq. dm. (1.9 to 37.2 amp./sq. ft.) with foil cathodes. The speed of rotation varied from 130 to 2160 r. p. m. Current efficiencies between 12 and 94 per cent were obtained and deposits containing from 0.06 to 0.77 per cent of iron. The cathodes used were of platinum in the form of foil for still experiments or when rotated at low velocities; of spiral wire for intermediate velocities; and small wires welded to a thicker wire for high velocities.

Except in the case of the foil cathodes, the cathode current density is not clearly stated, which prevents a critical discussion of many of the results when wire cathodes were used. The authors do not state whether they filtered the solutions after each experiment, or allowed a precipitate to accumulate in the bottom of the cells; from two to three cells were used in series, but it is not evident just how many times a given lot of solution was used. The solutions were not analyzed for iron, and lacking the above data it is somewhat difficult to discuss the results obtained in the light of the more recent knowledge of the action of iron and the effect of hydrogen ion concentration.

They found a surprisingly small iron content in the deposits, considering the high content of the anodes, when still baths were operated. Bagging the anodes or placing the cathodes in porous cups reduced the amount of deposited iron still further. Under such conditions, when the cathodes were rotated, the cathode efficiency decreased strikingly as the speed of the rotation was increased. Without some form of diaphragm between the electrodes, the iron content of the deposit increased when rotation

[10] D. F. Calhane and A. L. Gammage (Worcester Polytechnic Institute), A Study of the Causes of Impure Nickel Plate with Special Reference to the Iron. J. Am. Chem. Soc., 29, 1268 (1907).

was employed, but with a diaphragm, which was usually present, the iron content of the deposit was not greatly affected by rotation.

The conclusions of the authors, in part, were as follows: "Using the ordinary compound anode containing about 7.5 per cent Fe, the amount of this element present in nickel plate will average about 0.10 to 0.14 per cent.

"If the electrolyte is stirred or the electrodes rotated the amount of the iron impurity increases very considerably.

"If the anodes are surrounded by bags or any suitable filtering medium, the amount of the (above) iron impurity is cut down about one-half.

"It appears that iron to the extent of 0.04 to 0.05 per cent will appear in the nickel plate in spite of filtering septa, and is probably the result of primary deposition by the current.

"The use of bags over the anodes seems desirable, as they do not appreciably raise the voltage, and they keep the bath much cleaner and decrease the iron impurity in the nickel deposit by about one-half.

"The surprising deficiency of the nickel deposit measured in current used, when the cathode is rotated, is interesting and will be further investigated with other metals and their compounds. This deficiency has been found to depend essentially on the speed of rotation, increasing as the speed of rotation increases. Until further investigation no attempted explanation of this fact will be advanced.

"The total avoidance of small amounts of iron in the nickel plate does not seem possible with the anodes at present used in technical work."

Most of the deposits obtained by Calhane and Gammage are described as being without tendency to exfoliate. The salts used were tested for iron and found to contain only a trace. Many of the deposits on rotated cathodes were dark in color.

It is suggested that the best interpretation of these results is that although the anodes were high in iron very little of it dissolved, but most of it remained in the anode slime. This could have resulted from precipitation at a high pH caused by

a low anode current density. Very little iron being present in solution as $FeSO_4$, very little could deposit at the cathode, in spite of its strong tendency to do so. Stirring the solution, or rotating the cathodes, would keep anode slimes and precipitated basic iron in suspension and some would be occluded in the deposit, unless a diaphragm were used to keep such material away from the cathode. Increasing the speed of rotation above a certain point would not greatly increase the amount of suspended iron brought into contact with the cathode and, in fact, the results seem to show that the iron content of the deposits did not increase particularly at the higher speeds of rotation. In a short experiment in which the iron in solution comes principally from the anode, stirring will tend to bring it to the cathode faster than natural diffusion, and with or without a greater tendency for iron to deposit than nickel it would be expected that the amount in the deposit would increase. Another possible explanation for the small amount of iron in deposits is that the solutions may have been changed after each run (duration of 1 to 3 hr.) and hence the amount present in solution never became appreciable.

In spite of the fact that Calhane and Gammage checked the low iron content of deposits found by them by means of plating two platinum strips at a commercial plant, the latter deposits containing only 0.096 and 0.080 per cent of iron respectively, we are forced to conclude that their experiments did not reproduce conditions that now exist in commercial practice. The conclusion might be drawn from their results that even when using anodes high in iron, the deposits obtained in the still plating process would probably be practically free from iron. Such a conclusion would not be justified, however, because it would be at variance with practically all other available data. One deduction does seem justified, *i.e.*, iron is readily occluded in nickel deposits. Calhane and Gammage did not apparently consider that there was any reason to attribute the loss of current efficiency upon rotation to any action of the iron.

Bennett and associates,[11] in the course of investigations upon

[11] C. W. Bennett, H. C. Kenny and R. P. Dugliss (Cornell University), Electrodeposition of Nickel, Trans. Am. Electrochem. Soc. **25**, 335 (1914).

rotating cathodes, reviewed and extended the experiments of Calhane and Gammage, confirmed their discovery of the effect of rotation upon the current efficiency of nickel deposition and offered an ingenious theory to account for the results of both investigations. Bennett used a solution containing 0.405 *N* (80 g./L. or 10.7 oz./gal.) nickel-ammonium sulfate and 0.084 *N* (10 g./L. or 1.33 oz./gal.) nickel chloride, with the addition of ammonium hydroxide in some cases. The volume of electrolyte evidently never exceeded a few hundred cc. Experiments were made using anodes containing 0.14, 0.50, 0.75 and 7.6 per cent of iron. The cathode current density was 1.5 amp./sq. dm. (13.9 amp./sq. ft.) The effect of rotating the cathode was found to be similar to that of operating a stirrer in the cell, *i.e.*, agitation produced the result in each case.

Bennett further found a striking variation of cathode current efficiency during the progress of the deposition from either still or agitated baths. The cathodes were removed and weighed every few minutes or hours, according to the duration of a run. It was found that from one to several hours were required for the current efficiency to become constant at a maximum value.

The explanation offered by him for the various results obtained, based upon the hypothesis of the setting-up of an "alkaline film" at the surface of the cathode, is about as follows: The alkalinity results from the removal of hydrogen ions by deposition, and the arrival of ammonium (or sodium) ions by migration to balance the hydroxyl ions left by the hydrogen. In this film, nickel alone is able to deposit, and the current efficiency approaches 100 per cent in nickel as soon as the film is established. The alkalinity of the film may be and usually is quite different from that of the body of the solution between the electrodes. Stirring the electrolyte violently enough, by whatever means, tends to disrupt the film and thus lowers the current efficiency, by lowering the alkalinity and permitting the deposition of hydrogen ions.

Iron can not pass through the film and deposit because precipitation occurs. Agitation breaks up the film and allows iron to enter and deposit, or else allows mechanical occlusion to take place more readily. "The iron content of a deposit formed on

a rotating cathode is greater than that formed on a stationary electrode. This may be due to mechanical occlusions." "At the time the best deposit of nickel is being obtained it should be impossible to get iron deposited at the cathode unless it be by mechanical occlusion or deposition."

It is significant that in comparison with the results of Calhane and Gammage, Bennett found, under certain conditions, that a large amount of iron entered the deposit. Thus, in one experiment lasting 15 hours, in the still chloride bath mentioned, with a cathode current density of 1.5 amp./sq. dm. (13.9 amp./sq. ft.) the deposit contained 3.5 per cent of iron. The average cathode current efficiency was about 95 per cent. The anodes used contained 7.6 per cent of iron and the solution at the start was free from iron. Here, nearly half of the maximum amount of iron that left the anode entered the deposit.

The surprisingly low current efficiencies obtained by Bennett at the start of many runs, often 90 per cent or less, at a cathode current density of 1.5 amp./sq. dm. (13.9 amp./sq. ft.) makes the presumption strong that the pH of the electrolyte as prepared was extremely low in comparison with the usual commercial practice. The fact that an appreciable time was required for the current efficiency to reach a maximum (about 4 hr. in the case of the 15-hr. run mentioned above) does not seem to us satisfactorily explained by the alkaline film hypothesis. The cathode was frequently removed and weighed (necessarily after drying) and yet the cathode efficiency-time curve shows no abrupt breaks, although an alkaline film would have been destroyed at each removal of the cathode and restored at each return of the latter, but evidently with an appreciable time required for such restoration.

If the initial slow increase of efficiency were due only to the gradual formation of an alkaline film on the cathode, any sudden disturbance of the cathode would necessarily alter or destroy such a film, and result in an abrupt change in current efficiency, which was apparently not the case. While we believe that the maximum alkalinity of a solution is usually to be found at the surface of the cathode, and that the alkaline film hypothesis does

help to throw light upon some of the phenomena of nickel deposition, we are inclined to regard it as more likely that the increase of current efficiency during the period of deposition was due principally to a general increase in pH in the entire body of solution used, caused by the efficiency at the anode exceeding that at the cathode for some time after electrolysis commenced.

This gradual automatic rise of pH of the body of solution would tend gradually to raise the pH of a surface film of solution upon the cathode without any wide difference existing between the two pH values at any time. After the pH of the body of the solution had reached a maximum at equilibrium conditions there would be little further change in the surface film and the current efficiency would remain constant, which it was observed to do in the experiment mentioned, in which the efficiency remained at a maximum of 95 to 96 per cent for many hours.

Assuming a sufficient concentration of nickel there would seem to be no reason why a semi-independent alkaline film should not have continued to operate, and have raised the efficiency eventually to nearly 100 per cent, but this did not occur.

When Bennett added the most favorable amount of ammonium hydroxide to a lot of solution previous to electrolysis, the initial current efficiency was raised to a value between 95 and 98 per cent. Adding the ammonia raised the pH of the body of the solution, probably to 4 or 5, and electrolysis caused a further automatic increase to perhaps 5.5 or 6, resulting in a further slight improvement in current efficiency.

Among Bennett's conclusions, it is stated that: "The efficiency is dependent upon the degree of alkalinity of the cathode film." We would suggest amplifying by adding "and the degree of alkalinity of the cathode film is in turn dependent upon the degree of alkalinity of the whole body of solution and is probably never much above the latter." It is also stated that: "The alkaline solution film at the cathode may be disturbed and the efficiency of deposition decreased by stirring the solution vigorously." Bennett does not mention any troubles due to exfoliation, and states that "the iron content of the anode does not materially affect the efficiency."

Bennett, Rose and Tinkler[12] continued this investigation. They refer to the initially low current efficiency as follows: "When the electrolysis is started for the deposition of nickel, hydrogen ions, being present, are liberated first, and therefore the efficiency of nickel deposition is low. If the electrolyte and cathode be stationary there is an impoverishment of hydrogen, with a subsequent deposition of nickel at an efficiency which depends upon the impoverishment of hydrogen or upon the rate of bringing up of hydrogen ions to the cathode. This rate of bringing up hydrogen ions to the cathode may be affected in two ways. First the electrolyte or the cathode may be rapidly moved and therefore diffusion aided. Second, the concentration of hydrogen ions may be increased, therefore the rate of bringing up hydrogen ions increased, because more are present to be brought up."

If agitation operated simply by disturbing an alkaline film it should be possible to make an entire solution as alkaline at the start as the film itself, and thus prevent any effect due to agitation. In this way current efficiencies should be the same whether a bath was agitated or not, and be high at the start in either case. This was the plan of the second investigation.

The solution was of the same composition as that previously used. The volume employed was 120 cc., to which 1 cc., 5 cc. or 10 cc. of 1 : 10 ammonium hydroxide was added in different experiments. The anodes were electrolytic nickel containing 0.14 per cent iron. The cathode current density was 1.25 to 1.50 amp./sq. dm. (11.6 to 13.9 amp./sq. ft.) Runs of 4.5 hr. were made with two cells in series with a copper coulometer; the electrolyte in one cell was still and that in the other agitated by rotating the cathode at 1000 r. p. m. It was found that "if the solution is of the proper alkalinity the efficiency begins high, and is maintained at a fairly high value when the cathode is rotated."

Except in the case of the solution treated with 1 cc. of 1 : 10 ammonium hydroxide, however, the efficiency of the agitated bath never reached that of the corresponding still bath, but always remained below it. With an addition of 5 cc. of the ammonium

[12] C. W. Bennett, C. C. Rose and L. G. Tinkler, (Cornell University) Electrodeposition of Nickel, Trans. Am. Electrochem. Soc. 28, 339 (1915).

hydroxide, there was a constant difference of about 5 per cent, while with 10 cc. there was a still greater difference of about 20 per cent, in actual efficiency.

It seems to us that these experiments, at least, hardly do more than furnish qualitative proof of the hypothesis advanced. Agitation certainly had a marked effect by decreasing the efficiency, but increasing the alkalinity of the bath did not always compensate for the effect. It would seem that some other factors must be involved.

Bennett reasoned that in nickel cyanide solutions, where the hydrogen ion concentration is extremely low, rotating the cathode should have an effect the reverse of that observed in nickel sulfate solutions, *i. e.,* the efficiency should be higher when the cathode is rotated than when stationary, because nickel ions would be supplied much faster than hydrogen ions. This was tried and found to be the case. The initial concentration of nickel ions is so low in such a solution, however, that the efficiency obtained at 2000 r. p. m. was only 1.65 per cent.

Mathers and Sturdevant[13] attributed the effect of rotation upon current efficiency reported by Calhane and Gammage, and Bennett and his associates, to impurities in the bath, rather than to the disturbance of an alkaline film at the cathode. They emphasized the point previously discussed, stating: "If the lower yields which they obtained with the rotating cathodes were due to the more rapid bringing up of hydrogen ions, it follows that the addition of sufficient ammonium hydroxide should have eliminated the hydrogen ions and thus made the yields with both rotating and stationary cathodes the same. No such place was found."

Mathers and Sturdevant reported a number of experiments, using baths of 300 cc. and the same composition as those of Bennett (80 g./L. nickel ammonium sulfate and 10g./L. nickel chloride) with various substances added. A current density of 0.4 amp./sq. dm. (3.7 amp./sq. ft.) was used with the stationary cathode and 2.2 amp./sq. dm. (20.6 amp./sq. ft.) with the rotating cathode (2200 r. p. m.) Alternate measurements of

[13] F. C. Mathers and E. G. Sturdevant (Indiana University), Trans. Am. Electrochem. Soc., 30, 135 (1916).

current efficiency with stationary and rotating cathodes were made in the same bath. The results were summarized as follows:

"This paper shows that the impurities in the nickel salts are the cause of the low initial current yields with stationary cathodes, and the still lower yields with rotating cathodes. The following points are brought out:

"1. Free mineral acid can produce this lowering of yields, but the neutralization of the baths by boiling with nickel hydroxide did not overcome the trouble.

"2. The yields from baths electrolyzed continuously with rotating cathodes started low but reached values of about 97.6 per cent in 2, 4 and 5 hours respectively for baths of 100, 200 and 300 cc. made from commercial nickel salts. Similar baths made from purified salts gave yields of about 98 per cent for the first hour regardless of the volume. This shows that impurities produce all the lowering of the yields.

"3. The yields with stationary and with rotating cathodes are approximately equal in all cases where the baths are sufficiently pure. The addition of KNO_3 equivalent to 0.104 g./L HNO_3 lowered the yields more than any other impurity that was tried. Ferric salts, ammonium citrate or ammonium acetate lowered the yields, but ferrous sulfate up to 2 per cent was almost without effect.[14]

"4. Free boric acid lowers the yields somewhat when present in quantities greater than 2 per cent."

The increase of efficiency during the course of an electrolysis, or the "aging" of a bath, was thus attributed to the removal of impurities. "The continuous electrolysis with rotating cathodes removed the impurities quicker than with stationary cathodes. Some impurities remained in a bath even after many hours of electrolysis with a stationary cathode, hence a rotating cathode in such a bath gave a lower yield than with a stationary cathode, because the agitation of the solution brought the remaining impurities to the cathode. It was not feasible to age all of the

[14] Larger amounts of ferrous sulfate, and even very small amounts of ferric ammonium sulfate, did lower the yields considerably.

baths with rotating cathodes, hence in most of the tables the stationary cathodes show the higher values."

The nickel chloride used by Mathers and Sturdevant contained nitrate to the extent of 0.52 per cent as HNO_3, equivalent to 0.052 g./L. HNO_3 in the solution used. They state: "These results show that nitrate is the impurity that is responsible for a large part of the initial depression in the current yield." This fact, together with the further fact that current efficiencies over 99 per cent were seldom obtained in either still or agitated baths, even after many hours aging (*e. g.*, 15 to 60), emphasizes the

TABLE I.

Decomposition Potentials of Solutions.

Composition	Concentration *N*	Strip Cathode volts	Wire Cathode volts
$FeSO_4$	0.2	—0.925	—0.950
$FeSO_4$ ..... H_2SO_4	0.2 0.02	—0.96	—1.024
$NiSO_4$ ..... H_2SO_4	0.2 0.02	—0.792	—0.925
$FeSO_4$ ..... $NiSO_4$ ..... H_2SO_4	0.2 0.2 0.02	—0.796	—0.928

The potentials as given are referred to the calomel electrode as a zero of reference.

importance of using materials of high purity in such work. It seems established that the composition and purity of the bath have an important effect upon current efficiency, and that a lowering of efficiency by agitation cannot always be accounted for by a disturbance of the cathode surface film.

In a previous paper Mathers, Stuart and Sturdevant[15] had called attention to a method for preventing the precipitation of iron from nickel baths and noted a characteristic effect of iron upon the deposits.

[15] F. C. Mathers, E. H. Stuart and E. G. Sturdevant (Indiana University), Nickel Plating, Trans. Am. Electrochem. Soc., 29, 383 (1916).

"Ammonium citrate (0.2 to 0.3 per cent), a solvent for iron and nickel hydroxides, will entirely prevent the formation of a sludge in nickel plating baths."

"The ammonium citrate . . . . gives a deposit containing approximately as much iron as was in the anode. Using an anode containing 6.49 per cent iron, the deposit contained 6.23 per cent iron when ammonium citrate was in the bath, but only 3.31 per cent iron in a deposit from a similar bath containing no ammonium citrate. *This iron in the nickel deposit is one of the chief causes of the dark or bluish color.**

"The addition of 0.5 per cent ferrous sulfate to a bath containing citrate made the deposit much darker before buffing and more blue after buffing. Addition of another 0.5 per cent of ferrous sulfate made these changes more pronounced. *These cathodes were harder, less smooth and more difficult to buff.** Salts of the alkali metals, both organic and inorganic, darken the deposits largely through their action on the iron. With pure anodes, the darkening is much less or even absent altogether."

Küster[16] measured the decomposition potentials of solutions of iron and nickel with the results given in Table I.

Küster found that only nickel separated when a solution containing both metals was electrolyzed with a cathode potential only slightly above the decomposition potential of nickel sulfate. At cathode potentials intermediate between those of nickel and iron, the deposit began to contain iron. These initial experiments were made at extremely low current densities. In the absence of knowledge of widely different "reaction resistances" to deionization at the cathode, improbable at low current densities, the relationship found by Küster would seem to be logically indicated by his potential values.

Apparently subsequent to these original measurements of Küs-

* Italics by M.R.T.

[16] F. W. Küster. Über die gleichzeitige Abscheidung von Eisen und Nickel aus den gemischten Lösungen der Sulfate. Z. f. Elektrochem. 7, 688 (1901).

This does not appear to be Küster's original article, and further data are quoted under the following reference, which should also be consulted: M. Schlötter, Galvanostegie, I Tiel, Über elektrolytische Metallniederschläge, 244 *et seq.* (1910), (Monographien über angewandte Elektrochemie, XXXVII Band; Viktor Engelhardt).

ter, Toepffer[17] made a detailed study of nickel-iron alloy deposition, using current densities (0.7 to 7 amp./sq. dm.) comparable with commercial deposition practice. Under these conditions it was found, in general, that a greater proportion of iron was

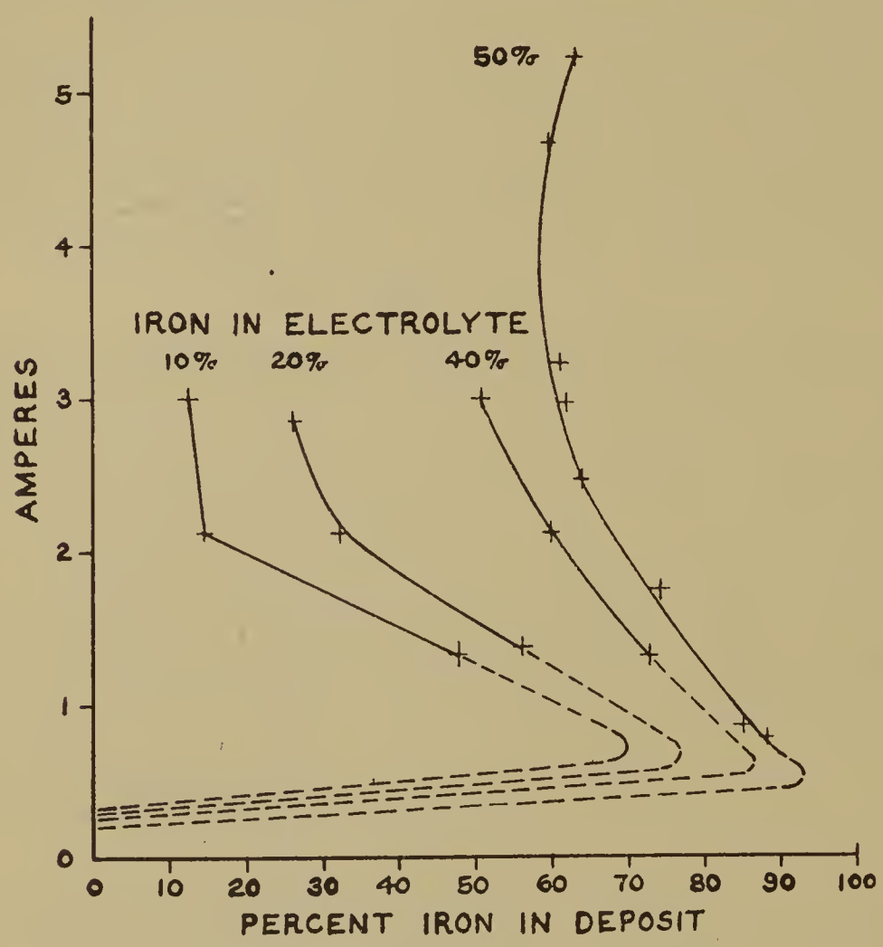


FIG. 1.

Adapted from Küster and Toepffer. Each curve is marked with the corresponding (constant) per cent of iron in the electrolyte, of the total metal content, 10, 20, 40 and 50 per cent respectively. Full lines represent Toepffer's measured values as given by Küster (Zeits. f. Elektrochemie, 6, 1889, 342, Fig. 107). Instead of showing the extrapolation of Toepffer's curves to 100 per cent iron in the deposit, we have added the dotted lines to represent approximately the correct continuation of the curves as established by Küster and discussed by him.

deposited in the alloy than was present in the solution used; *i.e.*, iron evidently deposited more easily than or in preference to nickel. A diagram of Toepffer's to illustrate this is reproduced

[17] H. W. Toepffer. Über die galvanische Ausfällung von Legierungen des Eisens und verwandter Metalle und über das elektrochemische Verhalten dieser Metalle. Dissertation. Breslau, 1899.

In lack of the original article, different portions of Toepffer's work will be found reviewed under the two following references and both of these should be consulted.

Z. f. Elektrochem. 6, 342 (1899).

M. Schlötter. Galvanostegie. I Teil, Über elektrolytische Metallniederschläge, 244 *et seq.* (1910). Monographien über angewandte Elektrochemie XXXVII Band; Viktor Engelhart.

in Fig. 1, in which the ordinates represent total current, but this is interpreted to mean current density in amp./sq. dm.; the abscissae represent the percentage of iron in the alloy obtained; the curves are each marked with the corresponding amount of iron expressed as a percentage of the total metal content of the solution. The latter was always 0.2 *N* in total metal (Fe + Ni), about 0.7 *N* in ammonium sulfate and probably about 0.002 *N* in free H_2SO_4. Similar results were obtained when the solution contained ammonium oxalate in place of ammonium sulfate. The time of deposition was usually between 30 and 60 min., but some times as long as 4 hr.

Moreover, the amount of iron in the alloy decreased with increasing current density (and cathode potential) as shown by the curves. No measurements were made at current densities below 0.7 amp./sq. dm., but the curves were extrapolated down to zero current density. The convergence indicated that only pure iron would be deposited at that point, at least if the solution contained 10 per cent or more of the total metal content as iron.

Similar relationships were found with a solution 0.2 *N* in total metal content as single sulfates and 0.002 *N* in free H_2SO_4, but there were more irregularities. In the latter solution, with 10 per cent of the total metal in solution as iron, the deposited alloy contained from 5.4 to 23.5 per cent of iron; with 50 per cent iron in the solution the alloy contained from 47.5 to 85.2 per cent; with 90 per cent iron in solution, the alloy contained from 90.3 to 97.3 per cent; the amount fluctuated somewhat irregularly as the current density varied from 0.7 to 7 amp./sq. dm., but the general tendency seemed to be for the amount of iron in the alloy to increase with decreasing current density. The time of deposition was usually between 5 and 50 min., some times as long as 5 hr.

It is apparent that the results of extrapolating Toepffer's curves to low current densities are not in agreement with Küster's earlier measurements at low current densities. Küster continues in his article[18] with a description of his later work, to bring the two researches into harmony as far as this range is concerned. He prepared solutions 0.2 *N* in total metal content of

[18] Z. f. Elektrochem. 7, 688 (1901).

nickel and iron as sulfates and 0.02 *N* in free H_2SO_4 (more acid than used by Toepffer), these contained respectively 10, 20, 40, 60, 80 and 90 per cent of the total metal as iron. The current densities were varied from 0.67 amp./sq. dm. (just below Toepffer's lowest measured value) down to 0.085 amp./sq. dm. The latter corresponds closely to the decomposition potential of nickel sulfate. "With potentials increasing above this deposition point it was shown, first, that iron separated in considerably less amount than nickel. The percentage of iron in the alloy then rose suddenly to a strongly inflexed maximum point, and from there fell off slightly. Here were joined the measurements of Toepffer, which show a continuous decrease in percentage of iron (in the alloy) with increasing current density."

Küster noted that the appearance of the deposit gradually altered from a matte-gray to a lustrous, shining surface, as the percentage of iron in the alloy increased. He believed that an alloy of the composition Fe_3Ni may be present under certain conditions. With regard to the relation between the relative amounts of iron in solution and deposit, the second phenomenon to be studied, he concluded that: "The deposit contains in general about 20 to 25 per cent more iron than the solution in the case of solutions containing over 10 per cent and less than 90 per cent iron (of the total metal content). The solution with 10 per cent iron gave a deposit with a maximum amount of 28 per cent iron, and that with 90 per cent iron gave a deposit with a maximum amount of 98 per cent iron. Further, it results from these measurements that iron, even if present in solution in preponderating amount, deposits at low potentials in lesser amount than nickel." Küster proceeds to discuss the possible bearing of reaction resistances and velocities at the cathode upon the separation of iron in relatively greater amount at higher current densities.

Summing up, we evidently may conclude:

1. The apparently discrepant results of Toepffer and Küster were finally harmonized by the latter.

2. Although Toepffer's curves strongly indicated the reliability of extrapolation, this, in effect, led to an entirely erroneous con-

clusion outside of the range of his actual experiments, which resulted in the apparent discrepancy.

3. With fairly large amounts of iron present in solution, and at ordinary current densities, Toepffer and Küster agree regarding a tendency for iron to enter the deposit in greater proportion than is present in the solution. Apparently, only nickel deposits at first from a mixed solution, as the current density is raised from extremely low values; then iron begins to deposit simultaneously in ever increasing amount up to a sharply-defined maximum, after which it continues to deposit simultaneously in decreasing amount. It would seem to be something of a problem to maintain constant the concentration of both metals in solution during such an investigation.

4. Neither Küster nor Toepffer apparently considered the possible effect of iron upon the exfoliation of nickel.

Kohlschütter and Vuilleumier[19] have studied nickel deposition by means of the contractometer, which consists of a thin platinum strip connected to a pointer and scale so as to magnify any movement. Metal is deposited upon one side only of the strip and the amount of bending toward the anode is noted. They found that adding $FeSO_4$ to a nickel solution increases the tendency for a nickel deposit to contract. The same is true, however, of many other substances. Vuilleumier[20] has predicted that such an effect is connected with a change in the internal structure of the deposit, which probably becomes more finely crystalline, lighter, harder and under greater internal stress.

Proctor[21] has stated that "The nickel deposit is usually whiter when it contains iron." In the electrotyping industry it has usually been held that iron makes a nickel deposit harder.

Schlötter[22] has stated that "The greatest difficulties met with in the nickel plating of metal articles result from the tendency of the deposit to peel off and be brittle. Recent investigations

[19] V. Kohlschütter and E. A. Vuilleumier. Z. f. Elektrochem. **24**, 300 (1918).
E. A. Vuilleumier, Metal Industry, New York. **19**, 419 (1921); **20**, 109 (1922).
E. A. Vuilleumier, The Application of the Contractometer to the Study of Nickel Deposition, Trans. Am. Electrochem. Soc. **42**, 99 (1922).

[20] Private communication.

[21] C. H. Proctor. Metal Industry (New York), **20**, 7 (1922).

[22] M. Schlötter, Ueber Vernicklung und Verkobaltung. Stahl und Eisen, **41** (1), 293 (1921).
Electroplating with Nickel and Cobalt (Special translation of above), Metal Industry (London), **19**, 447 (1921).

have shown that from solutions of iron-free salts deposits can be obtained showing no tendency to peel. In practice, it is not possible to keep the solutions absolutely free from iron. The nickel deposited from the solutions generally used absorbs hydrogen during deposition. This hydrogen, associated with a certain amount of iron in the deposit, is the cause of peeling in many cases. Adhesive deposits are obtained from warm baths; under these circumstances there is least absorption of hydrogen by the metal. With a bath at 70° to 80° C. the deposit contained 4.32 times its own volume of hydrogen, whilst at ordinary temperatures the deposit contained 13.57.

"The solution should contain a little free acid, which suppresses the absorption of hydrogen to some extent. Acidity and current density must stand in a certain relationship in order to obtain adhesive deposits. Low acidity and low current density give the best and most adhesive deposits.[23]

"If, on bending a nickeled article the deposit splinters, the bath contains too much iron as impurity.

"For the removal of iron, the bath is heated, and sodium or magnesium carbonate (better) added until the bath is neutral. When the bath has reached the boiling point ammonium persulfate is added in order to oxidize the iron present. As a rule, 2 g./L. is sufficient. The bath will again be acid after addition of the persulfate. More soda or magnesium carbonate must be added in order to render it neutral again. Since basic iron oxide is readily soluble in acids, it is not possible to precipitate the iron completely while the bath has an acid reaction. When the bath has been well boiled, the flakes of ferric hydroxide coagulate and settle to the bottom of the liquid. After removal[24] of the iron the bath is rendered slightly acid, after which it works just as well as a new bath.

"Peeling of the deposit may be caused by petroleum (often used for removing polishing materials adhering to the articles) in the bath."

Vuilleumier[25] has suggested a different method of removing

[23] Compare M. R. Thompson, The Acidity of Nickel Depositing Solutions *loc. cit.* (3), in which the quantitative relationship is shown.

[24] This is not considered necessary in order to prevent redissolving the iron, as will be discussed later. Removal of iron sediment may prove of advantage, however, in order to prevent its occlusion in the deposit. (M. R. T.).

[25] E. A. Vuilleumier. Metal Industry (New York), 20, 109 (1922).

iron from the nickel bath, when this is desired. The solution is agitated with plastic nickel carbonate, or the iron is oxidized more rapidly by means of barium dioxide (leaving insoluble barium sulfate) and then treated with the nickel carbonate. Ferric iron is completely precipitated and no metals are introduced into the solution.[26]

While both Foerster and Schlötter mention hydrogen and iron as each influencing the tendency of nickel deposits to peel or exfoliate, it seems evident that they expect best results when iron is absent.

The preceding discussion probably includes the most important papers bearing directly upon this subject, although we have not been able to prepare an exhaustive bibliography. For the more convenient consideration of the various subjects, we have neglected chronological order in some cases. Analyzing the various results and opinions as carefully as possible leads us to the following general conclusions:

1. There is little real evidence available in these references to show that iron influences exfoliation or "peeling" of electrodeposited nickel, in spite of some of the opinions expressed or inferences drawn.

2. There is considerable evidence to indicate that under certain conditions iron deposits preferentially to nickel from a solution containing both metals. In many of these investigations conditions were quite different from those usually found in commercial deposition, especially as regards nickel concentration and degree of acidity, or pH. Nevertheless, we are perhaps justified in concluding that something similar may be expected in commercial deposition. Several writers have found indications that precipitated basic iron compounds may be occluded in nickel deposits. Iron has been found to produce darker deposits, at least under some conditions.

III. EXPERIMENTAL WORK.

The experimental work at the Bureau of Standards had the following objects:

1. To ascertain if heavy nickel deposits could be made in the

[26] Some ferrous iron and usually any injurious amount of zinc or copper present as purity are also removed. (M. R. T.).

presence of iron, under definite pH conditions, without exfoliation.

2. To study the effect upon crystal structure of the co-deposition of iron with nickel, and from this metallographic work to infer the effect of iron upon the physical properties of the nickel.

3. To trace the conduct of iron, in general, in the nickel bath, and specifically to follow the action of any colloids by means of the ultra-microscope.

Our experimental work has been undertaken from a standpoint somewhat different (especially the regulation of pH) from that of previous investigators. The results are in general agreement with commercial practice.

The Hydrogen Ion Concentration of Iron Solutions.

The pH of a solution 0.1 *N* in $FeSO_4$ and 0.1 *N* in Na_2SO_4 in contact with freshly precipitated $Fe(OH)_2$ (obtained by adding NaOH solution) was found to be between 5 and 6, using the Gillespie method and brom-cresol purple as an indicator. The pH of a solution 0.1 *N* in $Fe_2(SO_4)_3$ and 0.1 *N* in Na_2SO_4 in contact with freshly precipitated $Fe(OH)_3$ was found to be about 3, using the same method and brom-phenol blue. These values correspond to the hydrolysis points of the respective salts in the above concentrations. The Na_2SO_4 present probably did not affect these results.

It follows that in commercial deposition, where the pH commonly ranges between 5.5 and 6.5, the latter is not far distant from the equilibrium pH of ferrous sulfate, but widely removed from that of ferric sulfate. The higher the pH, the greater will be the tendency for hydrolysis of ferric sulfate. The iron dissolved in the nickel bath will be mostly present in the ferrous condition, and as fast as oxidation occurs the ferric sulfate formed will probably hydrolyze and precipitate at once. While the course of this oxidation-precipitation may be written in various ways, the following equation represents the simplest final condition, neglecting the possible formation of basic sulfates (and borates).

$$4FeSO_4 + O_2 + 10H_2O = 4Fe(OH)_3 + 4H_2SO_4.$$

Free sulfuric acid is, therefore, released and the general tendency of nickel baths operated with anodes containing appreciable amounts of iron is to become more acid (lower pH) unless:

a. The anode current efficiency is higher than the cathode efficiency and sufficiently so to compensate for the acid liberated as above.

b. The bath contains nickel hydroxide or carbonate in suspension, or settled out at the bottom.

It is also obvious that if acid is added slowly to the bath and while stirring, there is little chance of a basic iron precipitate redissolving. Unless the latter comes into contact locally with solution of pH 3 or less, there will be little tendency for resolution and, if any iron does go back into solution locally, it will tend to hydrolyze and reprecipitate as soon as it mixes with the main body of electrolyte, which is at a considerably higher pH.

Preliminary Electrolyses.

The preliminary electrolyses were made in three cells connected in series, each containing 7 liters of solution of the composition stated below:

Composition of Electrolyte.

		g./L.	oz./gal.
$NiSO_4 . 7H_2O$ ..	1.00 *N*	140	19
H_3BO_3	0.25 *M*	16	2
NH_4Cl	0.25 *N*	14	2

In these experiments, iron salts were purposely added to the solutions in definite quantity, in order to determine the effect of excessive amounts of iron.

The nickel salts used were free from iron, copper and zinc. There was no addition made to jar No. 1. Thirty-five grams of $FeSO_4 . 7H_2O$, equivalent to 1 g./L. of ferrous iron, was added to jar No. 2. Twenty-five grams of $Fe_2(SO_4)_3$, equivalent to 1 g./L. of ferric iron, was added to jar No. 3. Electrolysis was conducted for 20 hr. at room temperature without agitation

Table II.

Data for Run A. (20 hr.)

Solution	Fe in Solution—g./L			Fe in Deposit Per cent	pH Before	pH After
	Before	After	Average			
1	0.00	0.26	0.13	0.40	5.00 (M.R.)*	4.95 (M.R.)
2	1.00	0.84	0.92	7.05	4.30 (M.R.)	4.90 (M.R.)
3	1.00	0.62	0.81	2.81	3.25 (B.P.B.)†	3.20 (B.P.B.)

* Methyl red.
† Brom-phenol blue.

Table III.

Iron Balance for Run A.

Solution 1.

Fe in solution at start	0.0 g.	Fe in solution at end	1.8 g.
Estimated Fe dissolved from anodes (maximum)	1.8 g.	Fe deposited (all from anodes)	0.2 g.
	1.8 g.		2.0 g.

Evidently no appreciable amount of iron precipitated from solution.

Solution 2.

Fe in solution at start	7.0 g.	Fe in solution at end	5.9 g.
Estimated Fe dissolved from anodes (maximum)	1.8 g.	Fe deposited	3.2 g.
	8.8 g.		9.1 g.

Average amount of Fe present during run, 6.45 g.
Fe deposited = 50 per cent of this amount.
Evidently no appreciable amount of iron precipitated from solution.

Solution 3.

Fe in solution at start	7.0 g.	Fe in solution at end	4.3 g.
Estimated Fe dissolved from anodes (maximum)	1.8 g.	Fe deposited	1.3 g.
	8.8 g.		5.6 g.
		Fe precipitated (by difference)	3.2 g.
			8.8 g.

Average amount of Fe present during run, 5.65 g.
Fe deposited = 23 per cent of this amount.
Fe precipitated = 57 per cent of this amount.

at a cathode current density of 1.2 amp./sq. dm. (11.1 amp./sq. ft.)

The anodes were cast anodes containing 94.0 per cent Ni, 4.2 Fe, 1.3 C, 0.2 Si and 0.2 Cu. Two anodes were used, with a total area front and back for the two about equal to the total cathode area. One sheet brass cathode 8 x 10 cm. in size was used. It was prepared by scrubbing with pumice and then treating in an electrolytic cleaner. The distance between the faces of the electrodes was 5 cm. No coulometer was used in series with the jars, so that the current efficiency was undetermined, but all three deposits were weighed and found to be practically the same. From previous determinations made on solutions of known pH, the current efficiencies in each jar must have been close to 100 per cent. The data for Run A are given in Table II.

The deposit from the first solution had the usual matte appearance, with a few pits. The deposit from the second solution was similar, but with much brighter edges; that from the third was less smooth than the others, of darker color and free from pits, although there was noticeable "gassing" during deposition (low pH). It was coated with a brownish precipitate readily soluble in dilute hydrochloric acid. There was no appearance of cracking or peeling in any case.

After the solutions had stood for three days they were used for a second run without further additions or treatment. All conditions were the same except that new and slightly larger cathodes were used, which resulted in a cathode current density of 1.0 amp./sq. dm. (9.3 amp./sq. ft.) The results of Run B are given in Table IV.

TABLE IV.

Data for Run B. (20.75 hr.)

Solution	Fe in Solution After Run g./L.	Fe in Deposit Per cent	Ni in Solution at End of Run		pH Before	pH After
			g./L.	*N*		
1	0.12	1.87	28.5	0.97	4.70 (M.R.)	4.70 (M.R.)
2	0.76	3.60	29.15	0.99	4.05 (M.R.)	4.35 (M.R.)
3	0.66	5.92	28.9	0.99	3.40 (B.P.B.)	3.65 (B.P.B.)

It was not possible to make an iron balance in this case, as the solutions had stood for three days between runs A and B and were not sampled immediately before run B. The deposits had a similar appearance to the previous ones. There was no cracking or peeling evident in any case.

In run A, the following average ratios of nickel to iron in solution and deposit are readily worked out, taking the total nickel in a lot of solution as 203 g. and the weight of each deposit as 45 g. The results are given below.

Metal Ratios.

	Ni/Fe Ratio in Solution	Ni/Fe Ratio in Deposit
No. 1	226/1	224/1
No. 2	31/1	13/1
No. 3	36/1	34/1

Even with very little iron present, as in No. 1, it deposited about as readily as nickel; in No. 2, the ferrous iron present deposited much more readily; in No. 3, the ferric iron deposited about as readily, probably after reduction at the cathode. Approximate calculations for Run B indicate that in all three cases the Ni/Fe ratio for the deposit was considerably less than for the solution, consequently it would seem that the tendency for iron to deposit in preference to nickel was operative in all three solutions by that time.

The pH values shown were those automatically assumed by the solutions as prepared or operated, and no attempt was made to alter them.

Some of the points brought out by these experiments include: The tendency for (ferrous) iron to deposit in preference to nickel; the effect of ferrous iron in brightening the deposit and ferric iron in darkening it; the slight tendency for ferric iron to deposit and great tendency to precipitate; the lack of effect of iron upon nickel current efficiency under the conditions; low pH associated with large amounts of ferric sulfate; the absence of any general tendency toward cracking, curling, peeling or exfoliation. There was little tendency for the solutions to become more

acid even in the case of the ferric solution, probably because they were well buffered with boric acid and because of very high anode corrosion.

Micrographs of the deposits made in these two runs, at a magnification of 100 diameters, are shown in Fig. 2 and 3. It will be noted that increasing the iron content, at approximately the same pH, causes the structure to become noticeably more finely crystalline. Compare deposits A-1 and B-1; A-1 and A-2; A-2 and B-2. Deposits A-3 and B-3 are both so finely crystalline as to give little distinction; the effect of the very low pH is here probably paramount. The pronounced porosity or tendency toward inclusions in the case of A-3 and B-3 should be noted. The finely crystalline structure indicates a metal probably lighter, harder, stronger, but more brittle, and under greater internal stress than does the coarsely crystalline structure, although we have not attempted to prove these changes in properties. The deposits from Run A had an average estimated thickness of 0.27 mm.; Run B of 0.25 mm. Specimens were cut from the central portions of the cathodes where the thickness is somewhat below the average. Etching was done by a mixture containing 50 per cent nitric acid, 25 per cent acetic acid and 25 per cent water (by volume).

Electrolyses at Constant pH.

Following these experiments a fresh lot of solution of the same composition as before was prepared, and several more carefully regulated electrolyses were conducted. A single cell containing 7 liters of solution was used in series with a copper coulometer. The anode and cathode current efficiencies were calculated from the weights obtained. The pH of the solution as prepared was brought up to 5.8 by the addition of 0.5 cc./L. of ammonium hydroxide, this pH representing approximately the degree of acidity prevailing in commercial practice.

The pH remained constant during these runs and it was unnecessary to do anything to regulate it. Measurements were made by the Gillespie method, using brom-cresol purple as indicator. Electrolytic anodes were used in order to obtain better control over the amount of iron present in the cell and to prevent

any possible effect of the other usual constituents of cast anodes upon the deposit. The electrolytic anodes were prepared by taking thin strips of commercial electrolytic nickel, containing only 0.14 per cent Fe, and plating with platinum anodes a heavy nickel deposit over these strips in a solution made up from very pure nickel salts free from iron.

In the succeeding runs in which these special anodes were used there was no appreciable corrosion of the base metal; practically only pure nickel dissolved. The anode corrosion obtained was nearly perfect, this result being in agreement with the work of previous investigators.[27] The submerged areas of the two anodes used were each 5.5 x 11.5 cm., and that of the single brass cathode was 11.0 x 16.0 cm., with a spacing of 7.0 cm. between faces of electrodes. The same pair of anodes was used in each of the four runs described below, with a new brass cathode for each run. No bags were used on the anodes. The cathodes were cleaned by scrubbing with pumice and then treating in an electrolytic cleaner. Electrolyses were conducted with a still bath at room temperature. The solution was not filtered again after starting the first run, and the same lot of 7 liters was used for all four runs. At the start of Run E, 40 g. of $FeSO_4 . 7H_2O$, dissolved in a little water, was added to the cell. This represented an addition of slightly over 1 g./L. of ferrous iron. No other addition was made during the runs. The solution acquired a slight turbidity during the course of Run D and was, of course, strongly turbid with precipitated iron during runs E and F. The data for the runs made are given in Table V.

Appearance of Deposits.

All four deposits had a matte surface and good color. In no case was there any evidence of cracking, curling or exfoliation. All the deposits showed a few pits, apparently due in part to a slow evolution of hydrogen, but principally to the collection and adhering of bubbles of gas, probably derived from air dissolved in the solution. The slight increase in temperature during elec-

[27] F. C. Mathers, E. H. Stuart and E. G. Sturdevant, Nickel Plating, Trans. Am. Electrochem. Soc., 29, 383 (1916); L. D. Hammond, University of Wisconsin, The Electrodeposition of Nickel, Trans. Am. Electrochem. Soc., 30, 103 (1916).

trolysis would tend to drive such air out of solution. Deposit E showed whiter edges and slightly less pitting than deposits C and D. Deposit F also showed white edges and the least pitting.

TABLE V.

Data for Electrolyses at Constant pH.

Run	C	D	E	F
Fe in Solution, g./L.:				
Before	.....	0.004	1.05	0.43
After	.....	0.004	0.43	0.28
Average	.....	0.004	0.74	0.35
Fe in Deposit, per cent	0.013	0.005	4.84	2.08
Weight of Deposit, g.	27.69	85.41	89.49	90.56
pH of Solution:				
Before	5.80	5.95	5.85	5.85
After	5.85	6.00	5.85	6.00
Duration of Run, hours	8.0	22.1	22.1	22.2
Av. Cathode c. d.:				
Amp./sq. dm.	0.91	1.02	1.08	1.10
Amp./sq. ft.	8.5	9.5	10.0	10.2
Av. Thickness of Deposit:*				
Millimeters	0.064	0.209	0.241	0.245
Inches	0.0025	0.0082	0.0095	0.0097
Cathode Efficiency, per cent	98.9	99.3	99.4	99.6
Anode Efficiency, per cent	99.7	100.0	100.6†	100.6†
Ni in Solution, g./L.:				
Before	.....	30.9	28.7	29.6
After	.....	31.8	29.6	29.3
Average Ratio of Ni/Fe:				
In solution	.....	.....	39/1	84/1
In deposit	.....	.....	19/1	46/1

* The figure represents the average measured thickness of the four sections of each deposit selected for microscopic examination.

† The anode efficiency was determined for the two Runs E and F combined; the figure represents the average for the two runs. The actual efficiency could not have exceeded 100 per cent. The result obtained was probably due to incomplete recovery of small particles of anode scrap from the bottom of the jar.

Structure of Deposits.

Samples were cut from all four cathodes and the structure of the deposit photographed at a magnification of 150 diameters

after etching as before. Two samples were cut from the central portion of each cathode, one from the upper half and the other from the lower half and the deposit on both sides of the cathode was examined. Views of these specimens are shown in Fig. 4, 5 and 6.

The character of the deposit obtained in runs C and D did not differ much from top to bottom or on opposite sides of the cathodes. Specimens from one side only were photographed. Deposits made in Runs E and F showed a greater tendency to develop pits after etching, on one side of the cathode (as will be discussed later), and there was possibly some variation in grain size from top to bottom on either side. All the specimens were photographed in these cases.

Deposits from the side of the cathode that was very slightly convex are designated "x"; those that came from the other (concave) side have no special designation. The convexity was due to the springing of the brass sheet used for cathodes and did not increase during deposition. It will be seen that the addition of iron caused the deposit to become more finely crystalline than pure nickel deposited under the same conditions. Such a result for a deposited alloy is in agreement with the usual effect of alloying two metals.

Colloids.

Samples of the solution before and after each run were examined under the ultra-microscope, in order to determine whether true colloidal matter, *i.e.*, small particles with Brownian movement, was present or made its appearance at any time. No significant amount was noted in any of the samples, although those from Runs E and F, in which a large amount of basic iron had precipitated, appeared to contain slightly more colloids than those from D and E. All samples were, of course, filtered before examination, so that visible turbidity was absent. The ultra-microscope may yet find some application in the qualitative or semi-quantitative checking up of the idiosyncrasies of plating baths.

Previous to these runs a number of samples of nickel solutions were examined; some of these were prepared for experimental purposes and some were submitted by commercial plants for co-operative tests. In several of the latter a relatively large amount

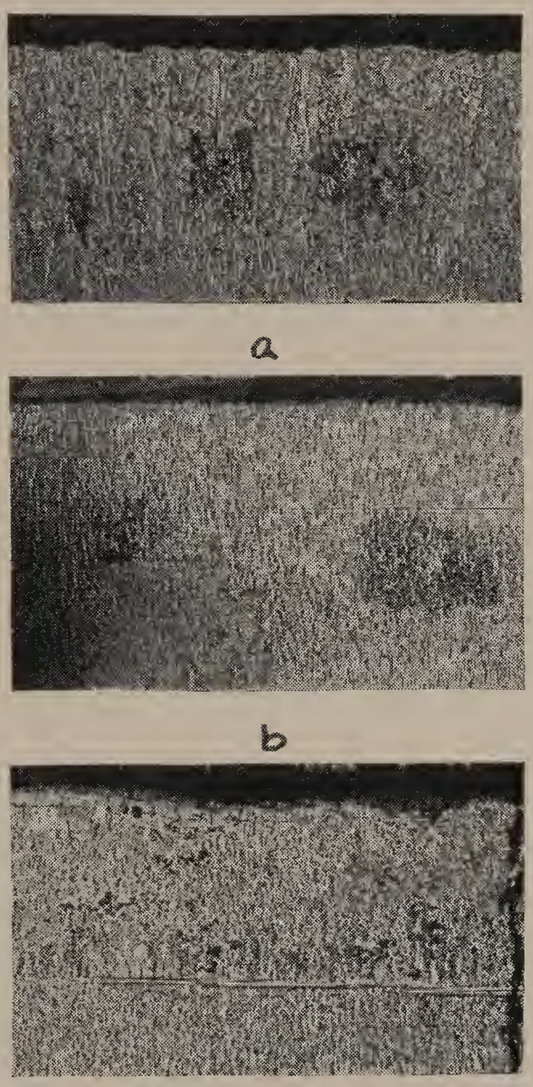


Fig. 2.

(a) Deposit A-1. 0.40 per cent Fe. pH, 5.00 - 4.95. x 100

(b) Deposit A-2. 7.05 per cent Fe. pH, 4.30 - 4.90. x 100

(c) Deposit A-3. 2.81 per cent Fe. pH, 3.25 - 3.20. x 100

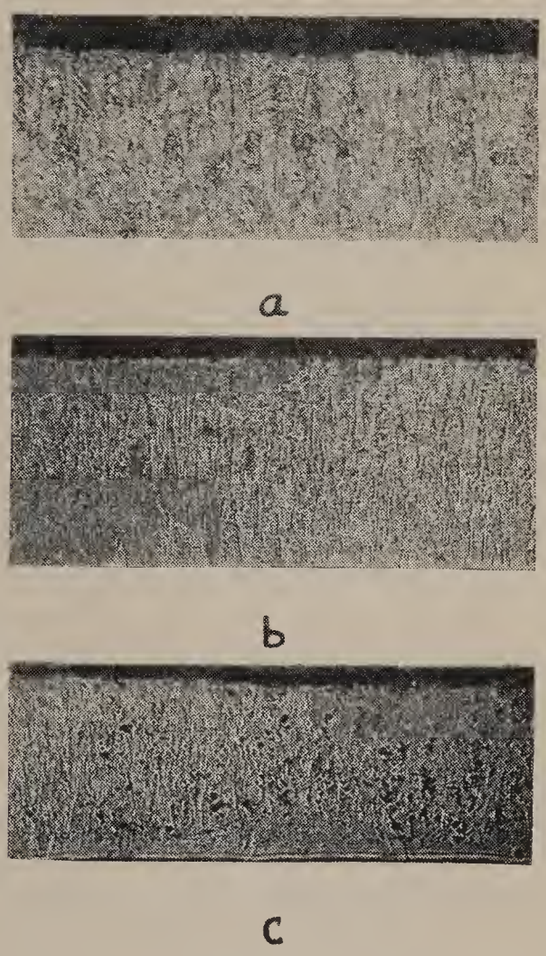


Fig. 3.

(a) Deposit B-1. 1.87 per cent Fe. pH, 4.70 - 4.70. x 100

(b) Deposit B-2. 3.60 per cent Fe. pH, 4.05 - 4.35. x 100

(c) Deposit B-3. 5.92 per cent. Fe. pH, 3.40 - 3.65. x 100

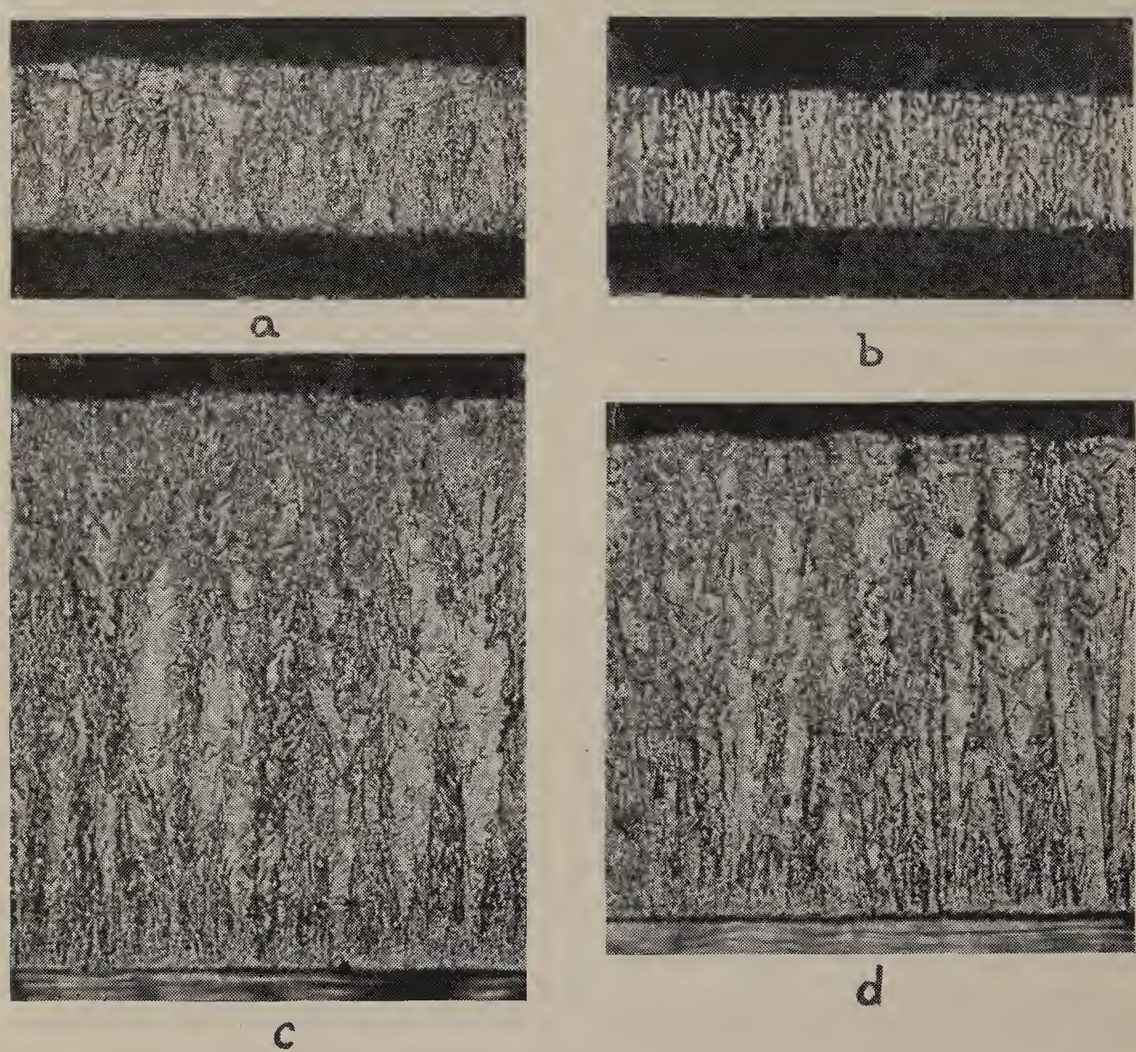


FIG. 4.

(a) Deposit C (top) (b) Deposit C (bottom)
0.013 per cent Fe. pH, 5.80 - 5.85. x 150
(c) Deposit D (top) (d) Deposit D (bottom)
0.005 per cent Fe. pH, 5.95 - 6.00. x 150

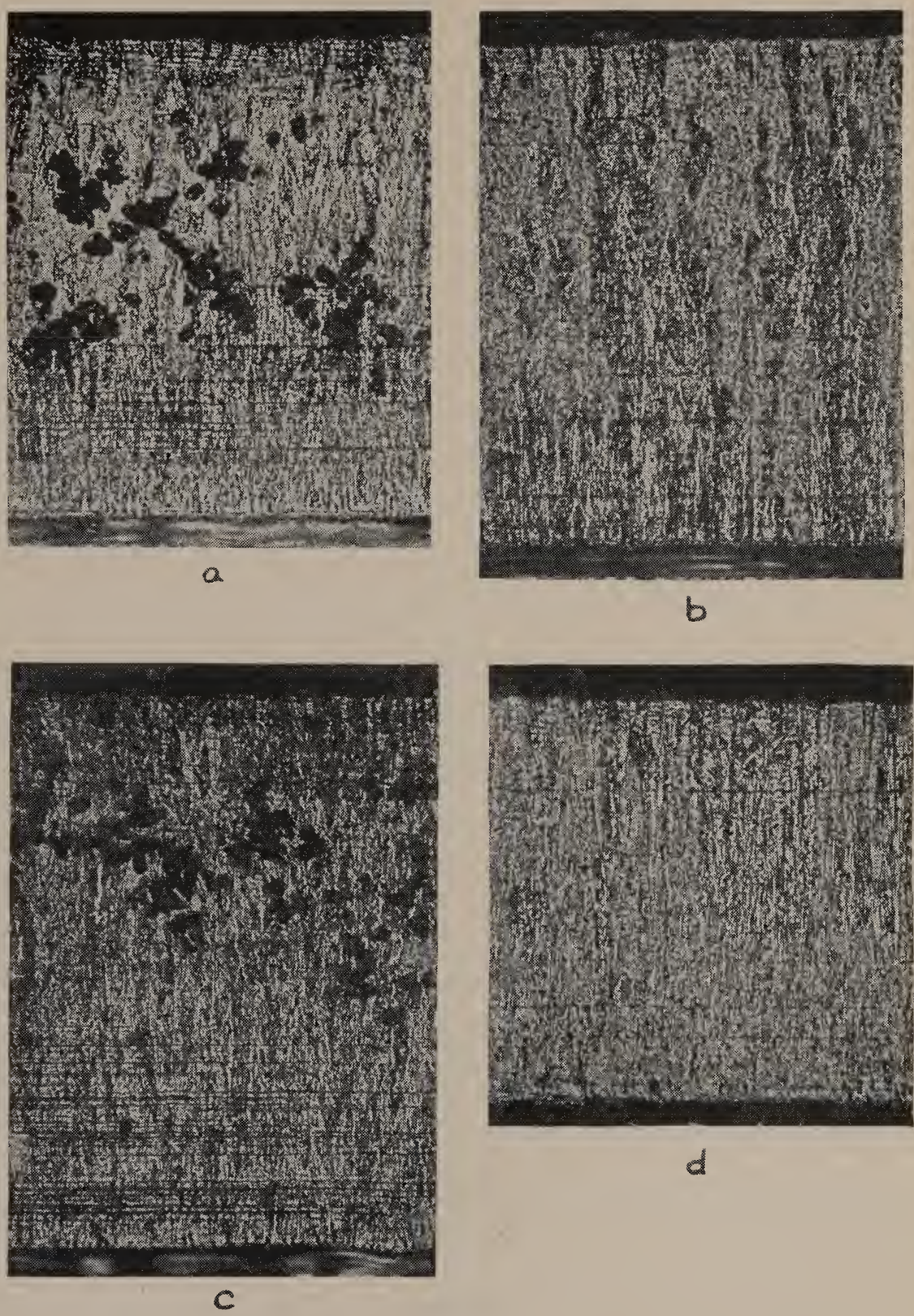


FIG. 5.

(a) Deposit E (top) (b) Deposit E (top "x")
(c) Deposit E (bottom) (d) Deposit E (bottom "x")
4.84 per cent Fe pH, 5.85 - 5.85. x 150

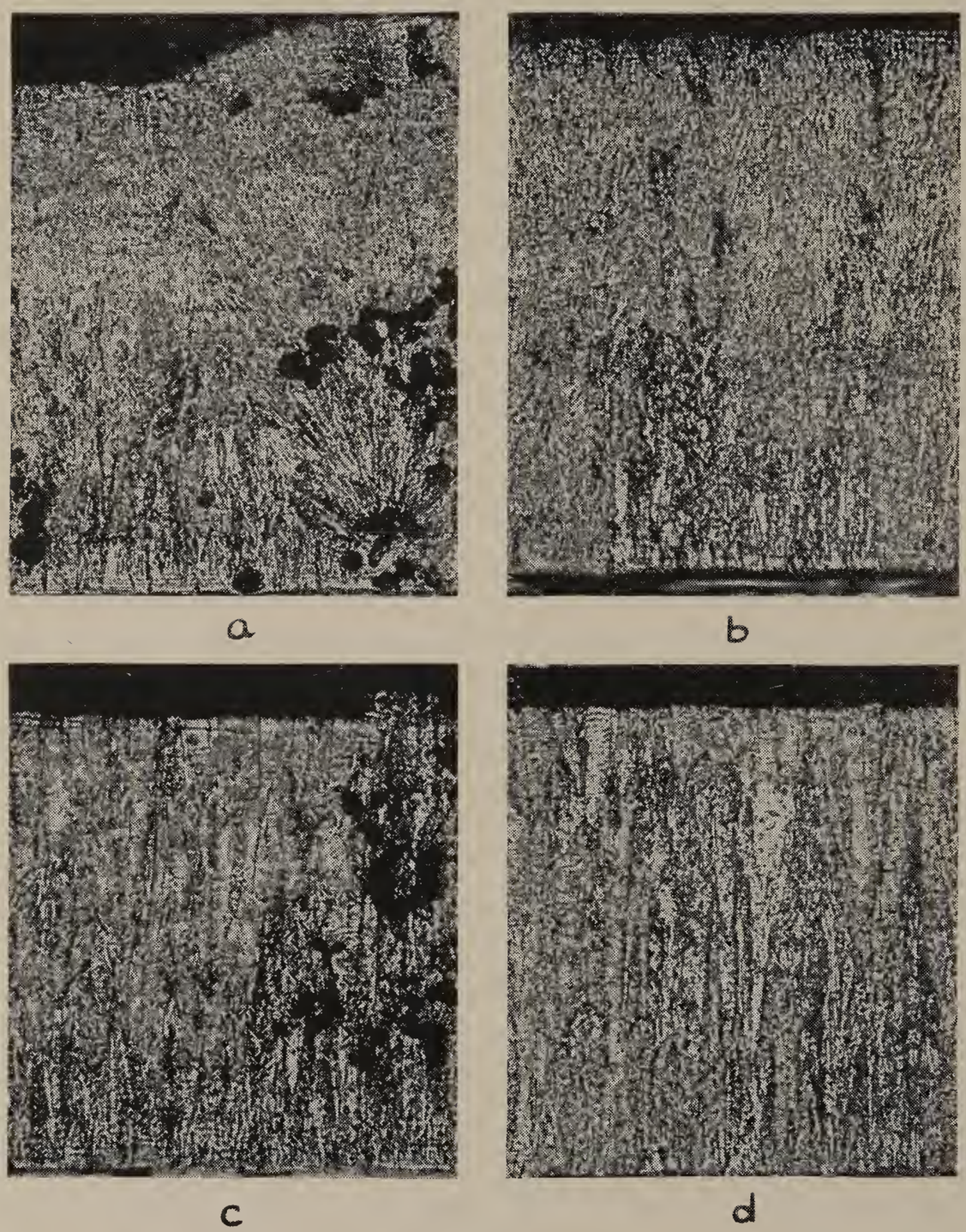


FIG. 6.

(a) Deposit F (top) (b) Deposit F (top "x")
(c) Deposit F (bottom) (d) Deposit F (bottom "x")
2.08 per cent Fe. pH, 5.85 - 6.00. x 150

of colloidal matter was observed; in the most striking case this seemed to parallel an unusually high content of iron (0.22 g./L.) in solution for this class of samples and a tendency for the bath to give deposits of a dark color and high in iron.

It was found that treating the sample with $Ni(OH)_2$, followed by settling and re-acidifying, removed the colloidal matter. Similar measures instituted at the commercial plant brought about an improvement in the deposits. It was thought that the source of the trouble lay in the use of an iron tank to hold cyanide for cleaning the work before plating and a stoneware tank was substituted, which eliminated further trouble.

Amount of Iron in Plating Baths.

The amount of iron present in some of the experiments described was probably excessive in comparison with that found on the average in commercial practice, although not in exceptional cases. The probable range of iron content of nickel baths that may be encountered remains to be discussed. Examination of a number of samples of nickel salts showed iron present from negligible amounts up to 0.13 per cent. In the latter case, if all the iron were soluble, a freshly prepared bath of *N* Ni content (about 140 g./L. of salts), would have contained 0.18 g./L. Fe.

Data obtained on a commercial plating bath containing chloride covering a period of two months, showed an average iron content of about 0.05 g./L. and a maximum of 0.10 g./L. In this case the nickel content was between 22 and 25 g./L. and the pH 5.5 to 6.0. Cast anodes of the 95 to 97 per cent grade were in use. Samples from several fluoride baths, used for preparing engraved printing plates, gave an average of 0.17 g./L. Fe, but larger amounts have been occasionally found. The electrolyte contained 55 g./L. Ni and 95 to 97 per cent anodes were used.

It is quite possible, at equilibrium conditions, for the ratio of nickel to iron in a solution to be much greater than that for the anodes being used, even if all the iron in the latter dissolves. All that is necessary is for iron to be eliminated as fast as supplied for any given ratio to remain constant. The preceding discussion makes it evident that the greater ratio for the solution is generally to be expected. Thus the concentration of nickel

and iron might remain constant in a given solution at 22 g./L. Ni and 0.055 g./L. Fe, a ratio of 400/1, the anodes being used containing 97 per cent Ni and 0.97 per cent Fe, a ratio of 100/1. The ratio for nickel to iron in the deposit could not, on the average, be less than 100/1, or greater than 400/1, but might have any value between these limits, according to the amount of oxidation and precipitation taking place.

It is impossible to discuss definitely the possibilities of accidental contamination of a nickel bath with iron. Evidently, through the use of salts containing an unusual amount of iron, or through insufficient rinsing after pickling or cleaning of the work to be plated, it would be possible to have somewhat more iron in solution than has been mentioned. Troubles with the deposit might then arise which could be very obscure, unless there was a knowledge of the general effects of iron upon nickel deposition.

Amount of Iron in Deposits.

The amount of iron found in deposits when iron is not purposely added to the bath will vary greatly with conditions. In general, the amount of iron in deposits will tend to approximate that in the anodes employed. Some very heavy experimental deposits made with anodes containing 94 per cent Ni and 4.2 per cent Fe contained from 0.9 to 2 per cent Fe. The solutions used contained 28 g./L. Ni. Two heavy deposits received from a commercial plant gave 0.2 per cent and 5.5 per cent Fe respectively, the latter being an exceptional case. The solutions here contained 22 to 25 g./L. Ni and 95 to 97 per cent cast anodes were used.

Occlusion of Iron.

Colloidal ferric hydroxide is known to migrate to the cathode. Although we have not as yet found evidence that it is present other than in exceptional cases, precipitated ferric hydroxide or basic salts of iron are invariably present in commercial deposition, unless continuous filtration of the bath is employed. It would seem possible for such precipitated material to become occluded in the nickel deposit, especially at places inclined to the vertical where particles could readily settle out and adhere.

Hughes[28] has noted striking amounts of inclusions in iron deposits, attributed to the presence of a basic precipitate. We have found it easy to obtain evidence of such inclusions in nickel deposits made on cathodes even very slightly inclined from the vertical, in the case of a solution very turbid with precipitated iron. While such inclusions might not affect the color of the deposit, it would be expected that they would increase its porosity and decrease its protective effect against corrosion of the base metal.

Evidence of inclusions is shown in the views of deposits E (top and bottom) and F (top and bottom) of Fig. 5 and 6. The cathodes used in these runs were sheet brass with a slight tendency to spring; consequently, one side in each case was actually (not purposely) very slightly convex and the other concave. Deposits made in solutions containing suspended iron precipitate show an increased amount of porosity on the side of the cathode referred to as concave. Neither side of the deposits made in iron-free solution shows much porosity. In the polished but unetched specimens nothing could be detected under the microscope which corresponded to the pits found after etching.

Precipitated, basic iron can hardly fulfill any useful function in nickel plating, and the preceding remarks indicate that the frequent filtration of a nickel bath is likely to have a beneficial effect upon its operation.

IV. CONCLUSIONS.

We have shown that iron has the following effects upon the electrodeposition of nickel, basing our conclusions both upon a review of the results of some previous investigators and also upon the results of experiments here presented.

1. The co-deposition of appreciable amounts of iron (2 to 7 per cent) with nickel, at a constant pH of the electrolyte, tends to give a more finely-crystalline deposit than is the case with pure nickel under similar conditions.

The "alloy" is presumably lighter, harder, more brittle and

[28] W. E. Hughes, On the Electrodeposition of Iron, Dept. of Sci. and Ind. Res. (British Gov't), London, Bulletin No. 6, 19 (1923).

under greater internal stress than pure nickel, which is relatively more coarsely crystalline.

The effect upon the nickel deposit is of the same type as that of an increase in hydrogen ion concentration of the solution (decrease in pH), and is apparently also primary.

Consideration of the relation between pH and the solubility of iron salts indicates that the lowest practicable pH that can be used would be best if iron is desired in the deposit. Electrotypers have sometimes added iron to the bath, but electrotyping baths are commonly found to be operated at a relatively high pH, say between 6 and 7. Dropping the pH to between 5 and 6 would aid in keeping iron in solution and would increase the amount deposited; whether such a course is in general advisable has not been determined during the present investigation.

2. The "alloy" tends to be whiter in color than pure nickel deposited under similar conditions.

3. If there is a precipitate of basic iron in the solution, it may become occluded in the deposit and cause a heterogeneous and probably porous structure. It is possible for the deposit to acquire a dark color, because this effect counteracts the preceding one.

Denser, more uniform deposits, affording better protection against corrosion, should be obtained from nickel baths which are filtered frequently in order to remove suspended basic iron precipitates.

4. Iron exhibits a greater tendency than nickel to deposit from a mixed solution, even when present in relatively small amount; a number of investigators are in agreement upon this point, even though the measurement of single potentials shows that iron is more electronegative than nickel, and it is also more active chemically.

5. Early views to the effect that iron is the principal cause of the cracking, curling, peeling and exfoliation of nickel deposits have not been sustained in the range of hydrogen ion concentrations studied (pH 3 to 6; in particular, 5.8 to 6.0). Both an increased iron content and an increased hydrogen ion concentration of the bath alter the structure in the direction tending

to favor such action, but apparently exfoliation in the presence of large amounts of iron is unlikely to commence if the hydrogen ion concentration is kept within bounds.

The latter factor appears to determine whether exfoliation will occur or not, and it is suggested that the difficulties of earlier investigators in this subject were not due to iron as supposed, but rather to the employment of excessively high hydrogen ion concentrations, perhaps a range of pH 2 to 3 being involved. Under such conditions, exfoliation is likely even when iron is absent.

Deposits of 0.25 mm. or thicker have been made without difficulty in the presence of a considerable amount of iron.

6. Observation of nickel solutions with the ultra-microscope has only occasionally indicated the presence of true colloids (Brownian movement) in significant amounts. The origin of such colloids could not be definitely determined, but a method suited to remove them from nickel electrolyte was developed.

The presence of an excessive amount of colloids is probably harmful to the color of deposits.

7. Suggested further work in this field includes:

a. Study of the efficiency with which iron dissolves from nickel anodes of various iron-nickel content.

b. Relative protection against corrosion given by nickel deposits of equal thickness but containing varying amounts of iron, as compared with pure nickel.

Acknowledgments are due to the following persons: H. S. Rawdon, Howard Scott and W. H. Mutchler for the preparation and criticism of micrographs of deposits; C. T. Thomas for analytical assistance; J. H. Winkler for preparation of deposits; Dr. Wm. Blum, who directed this investigation, for many suggestions; H. M. Johnquest, Geo. B. Hogaboom and members of the Research Committee of the American Electro-platers' Society.

DISCUSSION.

E. A. Vuilleumier[1]: About a year ago we ventured the opinion in "Metal Industry," that the peeling of nickel deposits is dependent upon two factors: The extent to which the metal

[1] Dickinson College, Carlisle, Pa.

as deposited tends to contract, and the degree of its adhesion to the surface plated.

The extent to which nickel as deposited tends to contract may be measured by means of the contractometer. Mr. Thompson has called attention to the fact that the published contractometric readings were obtained from solutions having an acidity considerably removed from the commercial range.

Guy Rolland, one of my students, has recently made some measurements that should be of interest in connection with the present paper. The apparatus used was similar to the one described at the Montreal meeting. The electrolyte was normal in nickel sufate of the highest purity, and quarter molar in boric acid. The anode, loaned by the Bureau of Standards, was of commercial cast nickel. The pH was adjusted by means of sulfuric acid, and measured according to the method recently developed by Mr. Thompson. The current density was 0.5 amp./sq. dm.

At a pH of 5.7 the deflection in 20 minutes was 5 mm.

At a pH of 6.1 the deflection in 20 minutes was 4 mm.

To a liter of the above solution, having a pH of 6.1, there were added 5 g. of $FeSO_4 \cdot 7H_2O$, equivalent to 1 g./L. of ferrous iron. The pH dropped to 5 g. In 20 minutes the pointer had moved 26 mm.—more than five times the normal deflection.

Mr. Thompson states in his paper that if the pH is properly controlled the presence of iron in nickel solutions does not necessarily cause peeling. What happens, however, when nickel is plated out from such a solution? Must we not conclude that it is under a great internal stress, under an enormous tendency to contract and peel? It is true that none of Mr. Thompson's nickel-iron deposits actually peeled, but was not that due rather to the second factor, a high degree of adhesion, obtained by Mr. Thompson?

Lack of adhesion is, no doubt, frequently due to a failure properly to clean the surface to be plated. Mr. Thompson has recently shown that if the pH of a solution is below about 4.5, or above about 6.5, that peeling is apt to occur. The presumption is that he used a uniformly excellent method of preparing his cathode. Unless this had been so, an element of great uncertainty would be introduced with regard to his conclusions as to peeling

or non-peeling. If, however, Mr. Thompson's method of preparing the surface to be plated was uniform, then must we not conclude that there is a second and more specific factor involved in the question of the degree of adhesion? This we have suspected for some time.

We called attention in "Metal Industry" to the desirability of measuring the degree of adhesion, especially with a view of ascertaining the relative efficiency of the various methods of cleansing the surface to be plated. Our plan was to measure the force necessary to pull away a definite area of plating. Our attempts to plate a suitable knob of metal on the surface have, however, not been successful. I would be thankful for suggestions as to possible methods for doing so.

E. O. BENJAMIN[2]: This paper seems to answer a question that has been created in my mind by past experience. In plating nickel on cast iron from a fresh double nickel sulfate solution, we have found considerable peeling, and a decidedly hard nickel surface. When the electrolyte has been in use for a period of time, we have found the presence of iron in the plating, but no peeling. In other words, there must be some relation between the base metal or iron and the iron in the solution. The plating out probably creates a bond by building up some of the iron crystals, which then are locked or held mechanically by the nickel coating. It would be quite interesting to know if any work has been done towards proving or contradicting this hypothesis.

C. P. MADSEN[3]: We have a method in the laboratory which will fill one of the problems asked for; that is, to precipitate a film of silver on glass, with the usual silver nitrate and reducing agent, and then attempt to plate nickel on it. If you can plate on that film, there is no contraction in the nickel.

COLIN G. FINK[4]: This subject of plating alloys instead of plating pure metals is becoming more and more important, not only on account of superior mechanical properties, but on account of resistance to corrosion of certain alloys. We find that we can plate certain alloys on base metals like iron, and get coatings

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[3] Consulting Engr., New York City.
[4] Head, Div. of Electrochemistry, Columbia Univ., New York City.

which resist the action of say the salt atmosphere, or acid atmosphere, better than the plate of either constituent.

W. Blum[5]: One practical problem which was suggested in Mr. Thompson's paper is the effect upon resistance to corrosion that may be produced by small amounts of iron in nickel deposits. All commercial nickel plating has iron in it and in some cases a relatively high percentage. Rapid failure of nickel coatings has at times been attributed to the presence of iron, although there have been no conclusive observations upon this point. The iron does, in certain cases at least, produce a denser, finer-grained deposit, which may be less susceptible to corrosion in spite of having iron in it. It is at least possible, therefore, that defects ascribed to the presence of iron are due more to the physical characteristics, such as lack of adhesion or porosity of the deposit, than to the actual susceptibility of the coating to chemical action.

M. R. Thompson: Adherence does have an important bearing upon cracking and curling, but all of the cathodes described were prepared by the electrolytic cleaner method, which probably gives the least degree of adherence as discussed in the paper just presented by Messrs. Blum and Rawdon. We do not feel that these deposits failed to crack and curl, on account of the tendency to do so being counteracted by an unusual degree of adherence. Nothing was done to favor such a result, as far as we are aware.

[5] Chemist, Bureau of Standards, Washington, D. C.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

THE CRYSTALLINE FORM OF ELECTRODEPOSITED METALS.[1]

By William Blum[2] and H. S. Rawdon.[3]

Abstract.

A simple theory of the probable mechanism of crystal formation in electrodeposition is outlined. The principal types of crystalline structures observed in electrodeposits are classified and the conditions which tend toward the formation of the different types are discussed.

I. INTRODUCTION.

In the voluminous literature on electrodeposition, reference has frequently been made to the reasonable analogy between the formation of crystals by electrodeposition and the usual processes of crystallization from solutions. Attempts to make useful deductions or valid predictions from such an analogy must of necessity involve some picture of the mechanism of the process by which the crystals are formed. The recent progress in the study of the constitution of matter suggests new considerations of these problems, and at the same time emphasizes the small amount of available accurate knowledge regarding the relations of atoms and electrons in even simple metallic structures.

It is not the purpose of this paper to discuss critically the various theories of electrodeposition that have been suggested, much less to propose or demonstrate any comprehensive hypothesis. A simple mechanism is depicted, which appears to be consistent with present views of atomic structure, and by means of which most at least of the known phenomena of electrodeposition may be co-ordinated. In the absence of conclusive proof, the most that can be claimed for the hypothesis here proposed is that it is apparently as valid as, and more simple than, those which

[1] Published by permission of the Director of the Bureau of Standards. Manuscript received June 27, 1923. [2] Chemist. [3] Physicist.

have previously been suggested. It is hoped that a consideration of these veiws will stimulate the research which is greatly needed to determine the validity of the various possible theories.

II. GENERAL PRINCIPLES.

It is generally accepted, on the basis of both microscopic and x-ray examinations, that all electrodeposited metals are "crystalline," that is, there is some definite geometrical arrangement or "orientation" of the atoms. Such terms as "amorphous" are therefore misnomers as applied to these structures. Similarly it may be assumed that all metal deposition upon the cathode results from the discharge of positively charged ions, usually of the metal which is deposited, although conceivably in certain cases the metal (*e. g.,* silver) may be deposited through the secondary action of some previously discharged more negative metal, (*e. g.,* sodium). If we consider the former method as typical, at least in simple salt solutions, the entire process of electrodeposition represents the change of positively charged metal ions into electrically neutral metal atoms having a crystalline orientation.

The actual steps by which this change occurs have been explained in different ways. In one theory[4] it is assumed that the electrical neutralization of the metal ion, that is, its combination with one or more electrons, occurs in the solution at a finite distance from the cathode, from which latter therefore electrons must pass into the solution. As a result of such neutralization, there is produced a supersaturated solution of metal atoms, from which crystals form just as from any other supersaturated solution. The applications of this hypothesis have been discussed in detail in the above cited papers.

In another theory[5] it is assumed, at least for the metals of the iron group, that the discharge of metal ions takes place upon the cathode in a haphazard way, and the discharged metal atoms remain in a dispersed or adsorbed condition upon the cathode for some finite period, after which they orient themselves to form crystalline structures.

[4] A. H. W. Aten and Louise M. Boerlage, Rec. Trav. Chim. Pay-Bas, 39, 720 (1920); W. E. Hughes, Bull. 6, Dept. Sci. and Ind. Res., London, (1922), Beama, 12, 215, (1923).

[5] V. Kohlschütter and E. Vuilleumier, Z. Elektrochem. 24, 300 (1918); H. Stäger, Helv. Chim. Acta. 3, 584 (1920).

We propose the theory that in most cases at least, the ion discharge and the metal crystallization constitute one and the same process, which may be pictured as follows. The neutralization of a given metal ion takes place upon the cathode surface, at a point at which the lowest discharge potential is required. This discharge potential at any point on the cathode is determined by (a) the "effective" metal ion concentration of the adjacent solution, and (b) the solution pressure of the metal at that point, which is determined in part by the orientation of the adjacent atoms.

It has been shown by x-ray studies that most of the metals which are electrolytically precipitable crystallize in the isometric system, usually with face-centered cubes. According to this conception the atom is the structural unit and there are no molecules in these metal crystals. The atoms (or atomic centers) are situated at points corresponding to the corners and face-centers of cubes, at distances from one another which are characteristic for each pure metal. No conclusive evidence has as yet been secured regarding the exact nature or magnitude of the forces which hold the atoms in position, or of the positions of any free electrons that may be present in the metal when a current is or is not flowing.

The forces which cause the atomic orientation or crystalline structure must be attractive, and must therefore counteract the tendency of the metal atoms to pass into solution as metal ions. In consequence the solution pressure of a metal crystal must be less than that of a single metal atom. Similarly the solution pressure of large crystals must be less than that of small cyrstals, because the internal attractive forces acting upon any atom on the surface must be greater in the large than in the small crystals. This conception is in harmony with the generally accepted fact that small crystals of any substance have a greater free energy and greater solubility than large crystals.

According to the above conception, the only solution pressure and corresponding normal single potential of any element which is characteristic and constant is that of the hypothetical single unoriented atom, or of a mass of metal consisting of unoriented atoms. The actual potential observed or calculated for a metal in

a given solution, is a function of this "primary" potential, and the change in potential corresponding to the decrease in solution pressure caused by the arrangement or orientation of the atoms in the crystal. The latter "correction factor" may be defined as the "orientation potential" of the metal in that form. As thus defined, the orientation potential is a measure of the deviation of the actual potential from the hypothetical primary potential. By definition this potential change is always positive, that is, any metal in a crystalline form must have a lower solution pressure, and hence a less negative single potential, than has the metal in an amorphous or unoriented form.

It is doubtful whether the relative or actual magnitudes of the orientation potentials can be estimated from existing data. The postulation of their existence is equivalent to a statement that the resultant of the forces which determine the orientation of atoms in a crystal may be expressed in terms of the electrolytic solution potential of the crystal. That the solution pressure and single potential of a metal vary with the state of division has been frequently observed,[6] and in all cases the potential has been found to be most negative for metals in the finest state of division. Differences as great as 0.03 v. have been recorded.[7]

III. NUCLEUS FORMATION.

The process of crystal growth in general consists in (a) the formation of nuclei, that is, of new crystals, and (b) the growth of existing crystals. With respect to any individual metal atom, these two processes represent respectively, (a) the discharge of an atom in a position independent of or unrelated to the arrangement or space lattice of the previously deposited atoms, and (b) the discharge in a position which represents a continuation of an existing space lattice. As frequently pointed out, the number of crystals produced in a given period in any process, such as electrodeposition, is a resultant of the relative tendencies for these two processes to occur. Any conditions that increase the rate of formation of nuclei, must tend to increase the number of crystals and *vice versa.*

There is no simple satisfactory definition of a crystal "nucleus."

[6] G. M. Lewis and W. N. Lacey, Jour. Am. Chem. Soc., 36, 804 (1914).
[7] F. Foerster, Electrochemie Wässeriger Lösungen, 3rd Ed. 1922, p. 181.

In the case of metals a nucleus probably consists of a single unoriented atom of the metal, unless some condition which predetermines the separation of that single atom at that particular point can be defined as a "nucleus." In the common case of silver deposition from a nitrate solution upon a platinum cathode, such as is employed in the silver coulometer, the platinum is "passive," that is, it has no measurable solution pressure. In consequence the potential of the platinum is that impressed upon it by means of the external e.m.f. If the platinum is thus made the cathode, it is negatively charged, and therefore probably has on the surface a relatively high concentration of electrons. Under such conditions it has been shown[8] that the number of nuclei (or at least of microscopically visible initial crystals,) formed in a given time increases (1) if the current density is increased, (2) if the metal salt (and metal ion) concentration is decreased, or (3) if the temperature is lowered. It was not found possible by these authors[8] to correlate the positions assumed by the individual crystals with any observed differences in the cathode surface or previous location of crystals on the cathode. Whatever conditions determine the location of crystal nuclei must therefore be of an evanescent nature. If we state that there must probably be momentarily at those points a higher concentration of electrons, we are merely restating the problem.

In a more recent study of silver nitrate solutions, Aten and Boerlage[9] found that the number of crystal nuclei increases if the current density is raised, or if any addition is made to the solution which increases the cathode polarization.

The influence of the various factors upon the number of nuclei may be explained in terms of the simple theory as outlined above. If a single atom has a higher solution pressure than a crystal, that is, an oriented group of atoms, it is obvious that a higher potential will be required to start a nucleus than to continue the growth of an existing crystal. All factors which tend to increase the difference in potential between the cathode and the solution must therefore foster the formation of nuclei, that is, of new crystals.

[8] E. B. Rosa, G. W. Vinal, and A. S. McDaniel, Sci. Paper 195, U. S. Bureau of Standards. (1912).

[9] *Loc. cit.*

The two simple methods of increasing the cathode potential difference are by (a) increasing the current density, and (b) decreasing either the actual or the "effective" metal ion concentration in the adjacent solution. Such a decrease in the effective metal ion concentration may be brought about (1) by diluting the solution, (2) by cooling the solution, (which retards diffusion and convection) (3) by adding a salt with a common ion, (4) by adding any substance such as a colloid which will hinder the processes of diffusion in the cathode film, (5) by increasing the viscosity, or (6) by forming complex ions. It is well known that the number of crystal nuclei can be increased by any of the changes just listed.

The preceding discussion of nucleus formation relates to deposition upon an inert cathode surface, the structure of which exerts no influence upon that of the deposit. Such a condition may be realized upon any metal surface if the latter is not "clean," that is, if a film of any sort masks the structure of the base metal; or if the surface of the latter is so nearly amorphous (*e. g.*, through rolling or burnishing) that no microscopic crystal structure is apparent. If, however, the base metal has been cleaned with acid, thereby removing any film of amorphous metal or of foreign material, the structure of the electrodeposit may be a continuation of that of the base[10]. To the extent that such crystal growth occurs, the initial process of crystallization by electrodeposition is essentially the same as that which occurs continuously during the deposition, and does not necessarily involve the electrolytic formation of nuclei.

IV. CRYSTAL GROWTH.

A single metal crystal may be defined as an aggregation of atoms, of which all parts have identical orientation. As previously indicated, the number of crystals produced in a given period is determined by the resultant of the respective tendencies for the formation of new nuclei and for the growth of existing crystals. It is possible therefore to classify the structures of all electrolytic deposits in three major groups, depending upon the relative magnitudes of these two tendencies. Within each group numerous varieties may be formed, depending upon secondary factors. The

[10] W. Blum and H. S. Rawdon, Trans. Am. Electrochem. Soc. 44, 305 (1923).

tentative classification shown in Table I has been arranged in the order of the diminishing tendency for the growth of crystals, as compared with the increasing tendency for the formation of new crystals. There is then a natural transition from each group to the next.

TABLE I.

Classification of Crystal Structures.

Group I—All (or practically all) of the initial nuclei or crystals continue to grow throughout the deposit.
- (a) Isolated crystals
  - (1) Symmetrical
  - (2) Acicular
- (b) Contiguous crystals
  - (1) Columnar
  - (2) Fibrous

Group II—Only part of the initial nuclei or crystals continue to grow.
- (a) Conical ("normal")
- (b) Twinned

Group III—No crystals continue to grow for any extended period.
- (a) Broken (compact)
- (b) Arboreal ("treed")
- (c) Powdery (spongy)

The above varieties of crystals are illustrated diagrammatically in Fig. 1 and photographically in Fig. 2. Obviously there may be numerous other kinds which represent either sub-varieties or transition forms.

The relations between the various typical structures may best be illustrated by a consideration of the factors which tend to produce each of these forms. It is not possible with existing data to predict for a given metal the type of crystals that will be formed under given conditions. It is possible, however, in most cases to predict the direction of the change in crystal type that will be produced when a given condition is changed.

Group I. In order for a given existing nucleus or crystal to grow, the potential necessary to deposit additional atoms upon that crystal must be lower than that required to deposit a single atom, that is, a nucleus, at any point adjacent to it. If the concentration of metal ions at the cathode surface were uniform, this condition would, according to the theory proposed always exist. But by the operation of deposition upon such a crystal the concentration of metal ions in the adjacent liquid is decreased, and if

there were no processes tending to restore the ion concentration, further deposition upon that crystal would soon cease.

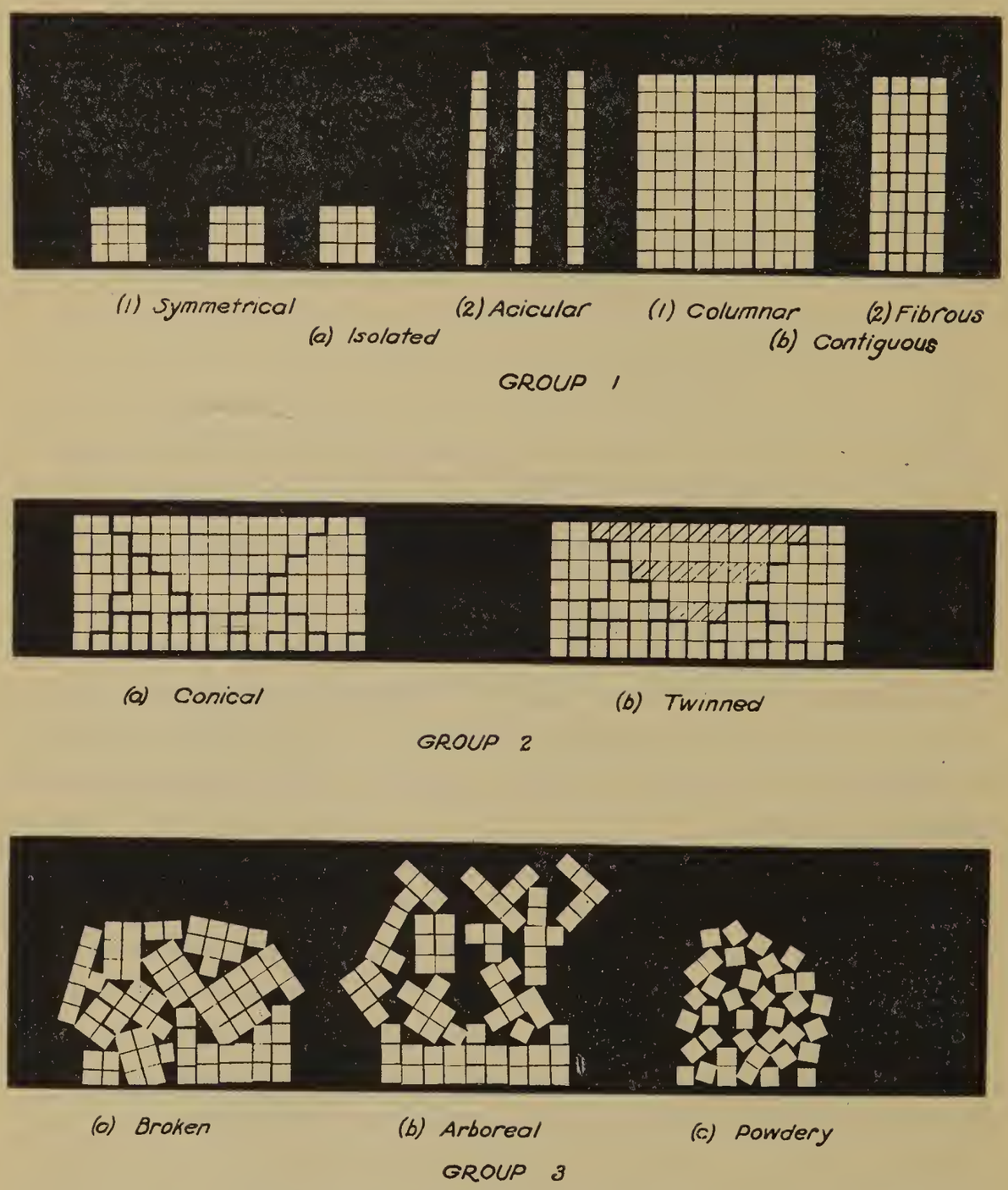


FIG. 1

Diagrammatic Representation of Principal Crystal Types.

The principal agencies which tend to replenish the metal ion concentration are (a) dissociation, (b) ion migration, (c) diffusion and (d) convection. It is possible to foster the growth of existing crystals by accelerating any of the above processes, and conversely to hinder crystal growth by retarding them.

The actual form and grouping of the crystals will depend in part upon (1) the number and spacing of the initial nuclei; (2) the effective metal ion concentration at the cathode; and (3) the potential gradient through the solution.

Among the factors which influence the convection, is the change in density of the solution. The greater the difference in density of the solution produced by the removal of the metal, the greater will be the tendency, to produce convection currents and thus maintain the metal ion concentration in the cathode film.[11]

In considering the effect of the potential gradient through the solution it is necessary to recall that at the cathode surface the lines of force are normal to the surface. This is a necessary condition upon an equipotential surface, such as exists in electrodeposition where the conductivities of the two media, (metal and solution) are widely different. In consequence the principal direction of growth of crystals is perpendicular to the cathode and not necessarily, as might at first be supposed, toward the anode. The greater the potential gradient through the solution, whether caused by a high resistivity or a high current density, the greater will be the tendency for the crystals to extend out from the cathode, as thereby the IR drop through the solution to that crystal is reduced, and the potential available there for metal deposition is increased.

The tendency of silver to form isolated symmetrical crystals from pure nitrate solutions is due in part to the relatively large change in density of the solution produced by the removal of the metal, and in part to the relatively high conductivity of the solution. Lead from nitrate solutions tends to produce isolated but acicular crystals. Lead nitrate also undergoes a large density change on removal of the metal, but owing to the relatively lower conductivity the crystals tend to grow out as needles. Acicular crystals of silver (Fig. 2b) may be formed at a high current density in relatively dilute silver nitrate solutions.

If the initial layer of crystals is practically continuous, as is the case with most metals such as copper, iron and nickel, the growth of all of these crystals will result in "columnar" forms, which may be designated as "fibrous" if the cross sections of

[11] H. E. Haring and W. Blum. Trans. Am. Electrochem. Soc. 44, 313 (1923).

the individual crystals are relatively small. Such forms are likely to be produced in concentrated simple salt solutions, at a low current density without agitation or at a higher current density with agitation.

In brief, structures of Group I may be produced from any solutions, or under any conditions, in which a relatively high metal ion concentration is maintained at the cathode. When such conditions exist, the current density-potential curve[12] is nearly vertical. Such curves may therefore aid in the prediction of the type of deposit that will be formed.

Group II. At a given stage in the electrodeposition, the metal ion concentration may not be maintained constant over the cathode surface, owing to unequal current densities or to variable convection currents. If however the composition of the solution and the other factors are such as to tend to restore the metal ion concentration, such temporary inequalities may be compensated. If not, one or more crystals which have momentarily received a higher current density will continue to grow more rapidly, at first in the direction of the potential gradient. But as a result of this increased current density the solution adjacent to the end of the crystal will become most rapidly depleted, and a time is reached when it is easier to deposit atoms on the sides of the crystal adjacent to the end than upon the end itself. In consequence the cross section of the crystal increases, and the adjacent crystals are literally "crowded out" by the "conical" crystals. It is at this stage that the greater orientation potential of the larger crystals becomes manifest, and retards the growth of the smaller adjacent crystals.

As thus defined, the crystals of Group II represent a transition or intermediate stage in crystal growth. The fact that they are formed from simple salt solutions of many metals such as copper, iron and zinc, within the range of conditions frequently employed in electrodeposition, has led to their designation as "normal" for those metals. Because they represent a transition stage it is hard to define briefly the conditions favorable for their formation. In general such forms will be produced under conditions

[12] For typical curves *cf.* Haring and Blum, *loc. cit.*

intermediate between those which yield deposits of Groups I and III respectively.

The intermediate character of this group justifies the inclusion in it of so-called "twinned crystals" such as are often produced from acid copper solutions. A single metal crystal has been defined as an aggregation of atoms of which all parts have identical orientation. A twinned crystal is one in which the orientation of the atoms in one portion is different from but bears a definite geometrical relation to that of the atoms in another portion. Its formation may according to this theory be pictured as follows. If in the growth of a given crystal, say of the conical type, the current density is increased, the cathode film is there depleted more rapidly, and in consequence further growth of that crystal is hampered and there is a tendency for a new crystal to form. The latter process requires, however, a relatively high potential.

The formation of a twinned crystal must require a lower potential than does that of a new crystal, because the orientation potential of the existing crystal exerts some effect upon the twin, though less than it would upon its own normal growth. Actually it has been observed by us that in the deposition of copper from acid sulfate solutions twinned crystals are formed at current densities intermediate between those which produce respectively "conical" structures and "broken" structures. In Fig. 2f is shown a twinned crystal produced upon a rolled copper surface treated exactly as in the investigation of the effect of the base metal,[13] but upon which the copper was deposited at about 8 amp./sq. dm. (74 amp./sq. ft.) instead of 0.8 amp./sq. dm. (7.4 amp./sq. ft.) previously used. In these later experiments it was found, as would naturally be expected, that at increased current densities the effects of the base metal structure were partly counteracted, but that growth of some crystals occurred and twinned crystals were frequently observed.

Group III. Whenever conditions become unfavorable for the growth of existing crystals, deposition must result in the frequent formation of new crystals. The term "broken" is here applied to all compact structures consisting of crystals started at intervals during the deposition period. The frequency with which new

[13] W. Blum and H. S. Rawdon, *Loc. cit.*

crystals form will determine whether such structures consist of relatively large crystals as from acid copper sulfate solutions, (Fig. 2g), or of very small crystals such as those from copper cyanide

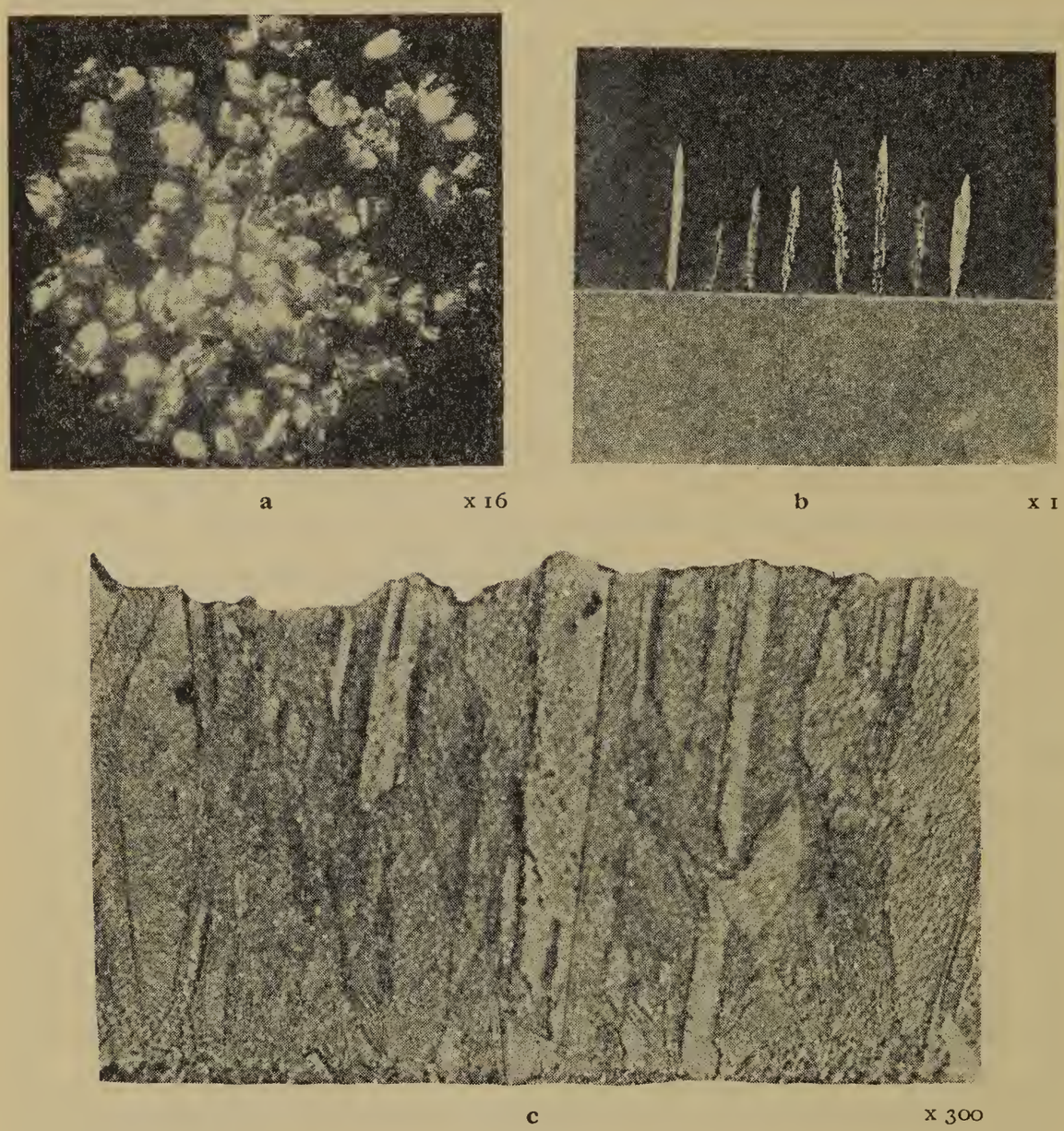


FIG. 2

Photographic Representation of Principal Crystal Types.

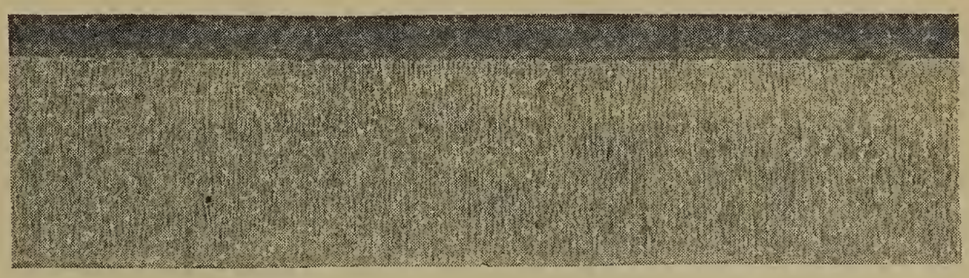
a. Isolated symmetrical. Silver from silver nitrate solutions.
b. Isolated acicular. Silver from silver nitrate solutions.
c. Columnar. Copper from acid sulfate solution.

solutions, which are difficult to resolve by present methods of etching and photography.

In general such forms are produced under those conditions which result in marked depletion of metal ions at the cathode, and in a corresponding increase in the potential required for metal

discharge at high current densities. Such deposits are often obtained by the use of a high current density in simple salt solutions, or even of low current densities in solutions containing colloidal addition agents or complex metal ions.

If the colloids increase the viscosity of the solution they will hinder convection and diffusion, and thus reduce the effective metal ion concentration at the cathode. If the colloid migrates to and accumulates near the cathode, it is likely to be adsorbed by the deposit, and thus hinder the orderly arrangement of the atoms



d x 100

e x 100

Fig. 2—Continued.

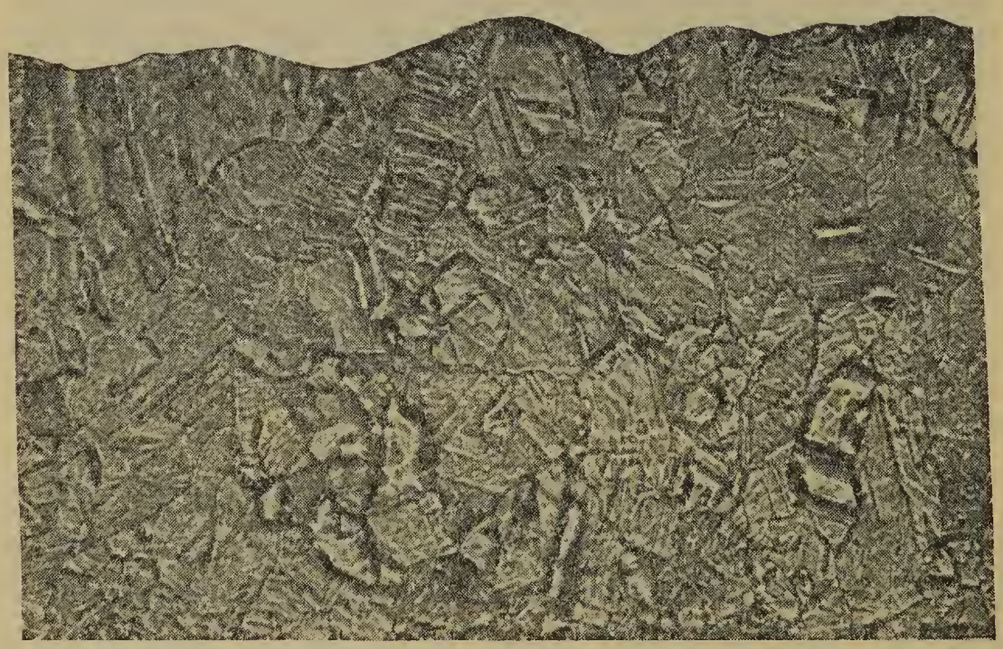
Photographic Representation of Principal Crystal Types.

d. Fibrous. Nickel from sulfate solution containing fluorides.
e. Conical. Nickel from sulfate solution containing chlorides.

and the growth of existing crystals. The specific effects of different colloids are probably due to differences in the degree and mechanism of their adsorption by the deposited metal. From complex salt solutions and those containing colloids the current density-potential curves are much inclined, which is evidence that in such solutions the "effective" metal ion concentration at the cathode rapidly decreases as the current density increases.

There has been considerable discussion in the literature upon the relation between current density and the size of crystals. The

f x 500



g x 300

Fig. 2—Continued

Photographic Representation of Principal Crystal Types.

f. Twinned. Copper from acid sulfate solution.
g. Broken. Copper from acid sulfate solution.

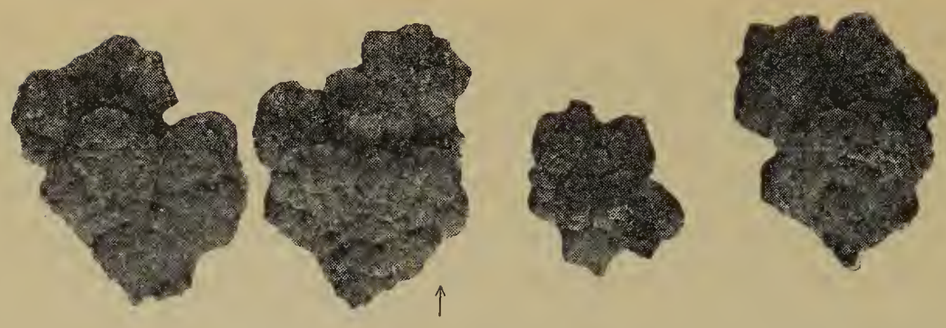
classification here proposed indicates that the *type* of crystal is more significant than the *size,* as obviously there may be relatively large or small crystals of any type or variety. Sieverts and Wippelmann[14] in their studies on copper deposition found that with increasing current density, the size of the crystals decreased to a certain minimum, after which there was an increase in crystal size. Hughes[15] in a study of iron deposition noted that as the current density was increased, the size of the crystals first increased, then decreased, and finally again increased.

It is believed that these observations may be harmonized if we consider the types of crystals probably produced in each case. Sieverts and Wippelmann obtained at a low current density "conical" (Group IIa) crystals of copper, and at somewhat higher current densities, "broken" (Group IIIa) crystals, which latter were, as is usually the case, smaller than the conical. Hughes, however, probably first produced fibrous or columnar structures (Group Ib) such are especially likely to form in iron and nickel solutions. An increase in current density then produced "conical" crystals, and a still further increase formed "broken" crystals.

The final increase in crystal size noted in both of the above investigations was apparently associated with the formation of rough or "treed" deposits. It is conceivable that a "tree", whether isolated or forming a part of a compact structure, which has started from a single nucleus may consist either (a) of one or at most a few large crystals, or (b) of a large number of small crystals. Sieverts and Wippelmann, and Hughes have accepted the former explanation.

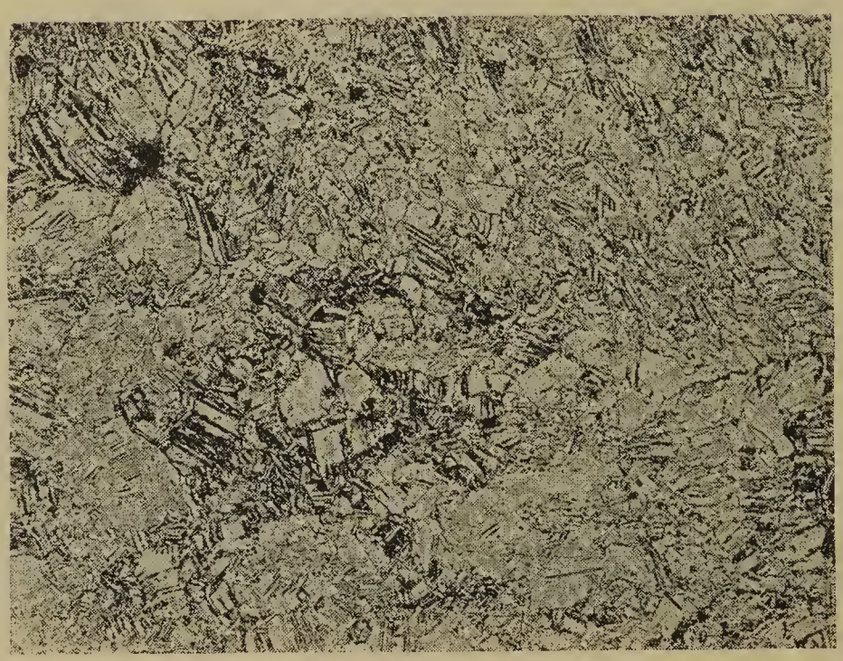
In order to throw light upon the structure of arboreal or treed deposits, the authors of this paper prepared several large copper trees by depositing copper from an acid sulfate solution at a high current density upon a copper cathode with numerous projections on the surface. Several such "trees" are shown in Fig. 3a. The specimen there marked with an arrow was cut through the longitudinal axis, mounted, polished and etched with a solution of ammonium hydroxide and hydrogen peroxide. Fig. 3b shows a photograph at a magnification of 2.5 and Fig. 3c at a

[14] Z. anorg. Chem. 91, 1 (1915) and 93, 287 (1916).
[15] *Loc. cit.*



a Natural Size

b x 2.5



c x 100

FIG. 3

Structure of Arboreal or Treed Deposits.

a. Copper trees.
b. Cross section.
c. Cross section.

magnification of 100. From both of these it is apparent that adjacent parts of the tree have entirely different orientations and that the tree consists of a large number of small crystals.

This observation was confirmed by means of an x-ray examination of this crystal, made by R. W. G. Wyckoff of the Geophysical Laboratory, Washington, D. C., to whom the authors desire to express their appreciation. He found that the specimen yielded on each of two polished planes at 90° to each other, a typical powder photograph, which shows that it consisted of a large number of small crystals, among which there was no favored orientation.

These results indicate strongly that the arboreal structures produced at high current densities, or in solutions having a high resistivity, or from those containing certain addition agents, consist of small crystals and owe their form to the great depletion of the cathode film, and the high potential gradient through the adjacent solution. In consequence of the former effect, new crystals are constantly formed; and because of the latter, the crystal aggregate tends to grow out into the solution. It is therefore probable that after broken crystals are once formed a further increase in current density always decreases the size of the individual crystals.

This conclusion is rendered more probable by the fact that if the current density is still further increased, the deposit always consists of spongy or powdery masses, of which the individual crystals are exceedingly small. The formation of such deposits is epecially probable when either by increase of current density or decrease in metal salt or ion concentration, the cathode efficiency is so diminished that hydrogen is liberated in appreciable amount, and thus actually separates the crystals.

Whenever hydrogen is discharged, especially from nearly neutral solutions, the film of solution at the cathode tends to become alkaline, in consequence of which metal hydroxides or basic salts may also be precipitated, and thus contaminate the deposit and insulate the crystals or at least hinder their growth.

In the preceding discussion, it is shown that the major effects of changes in the different operating conditions upon the crystal structure can be explained by means of the simple theory proposed. The primary factors which govern the structure are:

1. The discharge potential of metal ions at any point on the cathode, which is determined by (a) the primary solution pressure of the cathode metal, (b) the structure and orientation potential of the cathode and (c) the "effective" metal ion concentration in the solution adjacent to the cathode.

2. The potential gradient through the solution near the cathode surface, which is a function of (a) the current density and (b) the resistivity of the solution.

If the above theory is correct, factors such as current density, temperature, agitation, etc., can affect the structure of the deposit only so far as they modify the potential relations. The rate of deposition of metal is, by definition, a function of the current density and metal cathode efficiency, the product of which represents the "effective current density." It is independent of other factors such as the temperature or composition of the solution, except as these factors affect the cathode efficiency.

The actual rate of metal deposition at any given current density is usually under otherwise uniform conditions equal to or greater than the rate at any lower current density, even though the cathode efficiency may be lower at the higher current density. A reduction in cathode efficiency below 100 per cent is an evidence that in the film of liquid adjacent to the cathode the effective metal ion concentration is insufficient to satisfy the current density then applied.

A still further increase in current density cannot result in any further depletion in metal ions, unless it removes metal at a higher rate, or unless metal ions are removed by some secondary reaction such as the precipitation of a basic compound. Most of the "excess" current is consumed in the evolution of hydrogen. The convection produced by such evolution must tend to increase the effective metal ion content of the cathode film, and thus permit the metal to be deposited more rapidly than when there is no such convection.

A decrease in cathode efficiency and corresponding hydrogen evolution may affect the structure of the deposit either by (1) increasing convection currents and thus increasing the effective metal ion concentration at the cathode, (2) dissolving in or alloying with the deposited metal, which is likely to occur with iron

and nickel and to produce very fine grained brittle deposits, or (3), interfering mechanically with the growth of crystals and actually separating crystals or crystal aggregates and forming a non-coherent powdery or spongy deposit.

The effect of one or more changes in operating conditions is determined by the resultant of their influence upon the potential relations. In principle, therefore, we may expect to produce upon the same base metal similar crystalline forms whenever the cathode potential is the same, whether secured with a low current density in a dilute solution, with correspondingly higher current density in more concentrated solutions, or with still higher current density in agitated solutions or by any other means, provided the potential gradients through the solution are the same in each case. Extensive experiments might be required to realize such conditions in actual deposition.

TABLE II.

Direction of Effects Upon Structure.

Change in Operating Condition	Change in Structure Group
Increase metal salt concentration.....	III → II → I
Increase metal ion concentration.....	III → II → I
Agitate solution.....	III → II → I
Elevate temperature.....	III → II → I
Increase conductivity of solution.....	III → II → I
Add colloids to solution.....	I → II → III
Increase viscosity of solution.....	I → II → III
Increase current density.....	I → II → III

In Table II, the probable direction of the effects of the principal variables is predicted in terms of the typical structures.

It is recognized that many observations upon electrodeposition may not apparently fit into the above tabulation. One difficulty is that many such records are of isolated experiments, from which no direct comparisons may be made. Another is that many of the photographs exhibited, including some from this laboratory, represent only the surface appearance of the deposits, and furnish no direct evidence regarding the internal structure. Wherever possible, therefore, the cross section of the deposits should be studied. As pointed out by W. E. Hughes,[16] however, there is a

[16] Trans. Am. Electrochem. Soc. 41, 317 (1922).

close relation between the internal structure and the surface aspects, and in some cases at least the former can be predicted from the latter. Even with so common a metal as copper, upon which so many researches have been published, no single investigation has included the effects of each of the variables under otherwise uniform conditions. There is a great need for a comprehensive systematic research of a number of metals, from which alone can any conclusive deductions be made.

In certain cases a given change may produce effects which tend to counteract each other. Thus the addition of sulfuric acid to copper sulfate solutions increases the conductivity and decreases the metal ion concentration. In such cases it is difficult to predict the actual effect, which will be a resultant of these two factors.

Among the factors upon which it is hard to generalize, is the effect of hydrogen ion concentration. In acid solutions such as of copper sulfate, it is probable that the effects of sulfuric acid are due principally to the change in conductivity and metal ion concentration, rather than to any specific effects of hydrogen ions. In nearly neutral solutions of iron and nickel, slight changes in acidity have profound effects. In such solutions a moderate increase in acidity (decrease in pH) tends toward the formation of bright fine grained deposits, but the exact cause of such a change has not been determined. Further studies on the relations between pH and the cathode potential may throw light on this subject.

One of the chief arguments in favor of the theory that the metal atoms are first discharged and subsequently orient themselves is the well known tendency of metals, especially nickel, to contract during deposition,[17] which phenomenon has been exhaustively studied by Kohlschütter and his associates. It was found that the contraction was increased when the current density was increased, when the temperature was decreased, when the hydrogen ion concentration was increased up to a certain point, or when foreign metals such as iron were present in the deposit. In all these cases the deposited metal was more finely crystalline.

[17] Kohlschütter and Vuilleumier and H. Stäger *Loc. cit.* and E. A. Vuilleumier Trans. Am. Electrochem. Soc. **42**, 99 (1922).

The above facts can be explained in terms of the theory of direct deposition. In addition to those forces which hold together the atoms in the form of crystals, there must be, in all coherent deposits, intercrystalline forces. These become manifest as soon as any two crystal surfaces approach closely, that is, within distances comparable with the atomic spacing. The tendency of any such intercrystalline forces will be to draw the crystals together, that is, to cause contraction. The extent of such contraction for a given metal must then be a function of the total surface of the crystals in contact. Deposits consisting of a large number of small crystals, either of the fibrous type of Group I, or of the broken type of Group III, must have a much larger intercrystalline surface per unit mass than coarse grained deposits, which is in harmony with the observed tendencies to contract.

The decrease in contraction observed when the thickness of the deposit increases is in accord with the usual tendency of a certain portion of the crystals to grow and to crowd out others, and thus to increase the average size of the crystals and thereby decrease the intercrystalline surface per unit mass. If therefore as is here postulated, the tendency toward contraction is a function of the intercrystalline surface, all factors which increase the latter will increase the tendency to contract and *vice versa.*

The fact that metals such as nickel and iron show a much more marked tendency toward contraction than other metals, such as copper, may be due to some specific effect of the hydrogen that may be absorbed by the former metals, or it may be associated with their high tensile strength. When metals which tend to contract are deposited upon a rigid surface, the elastic limit of the deposited metal may be exceeded, and the resultant sheet may remain flat even when it is detached from the base metal. Bending of a given cathode during deposition is most easily effected with metals of high elastic limit, such as iron and nickel.

The fact that silver can be deposited[18] from dilute solutions in the form of black finely divided particles, which undergo a change to the white crystals on standing, may be connected with the greater solution pressure of the finely divided metal, and the consequent tendency to form local couples in which the finest par-

[18] V. Kohlschütter and associates—(4 articles). Z. Elektrochem. 19, 161-184, (1913).

ticles serve as anodes. This behavior does not of itself justify the assumption that, under the usual conditions of deposition, silver or other metals are first liberated in an amorphous form and then undergo a transformation into the crystalline state.

The recent observation[19] that, in certain cases at least, the formation of crystals is a discontinuous process consisting of growth, not by individual atoms but by layers of atoms, may, if confirmed, also be explained as well by the theory here proposed as by that of atomic discharge and subsequent orientation. If we assume that the metal crystal is made up of face-centered cubes, it is conceivable that at a given instant a certain face may be completely filled with such cubes. Under such conditions it is obvious that a higher potential or greater metal ion concentration will be required to start a new cube, or a new layer, than was required at any intermediate stage during the formation of the previous layer.

If deposition momentarily ceases upon that crystal, the temporarily depleted metal ion concentration will tend to be restored until it reaches such a value that the applied potential is adequate to start a new surface. As soon as this occurs, the rest of the layer may form rapidly, as the metal ion concentration is now in excess of that required for continued growth at the potential applied. If then the process of electrodeposition on a given crystal surface is rhythmic, it may depend upon a momentary increase of metal ions in the cathode liquid film instead of an accumulation of metal atoms on or in the cathode surface, as postulated by Volmer. A study of deposition upon a single crystal face would probably determine whether the electrodeposition is actually discontinuous.[20]

SUMMARY.

1. A simple theory of the mechanism of crystal formation in electrodeposition is outlined, according to which,

a. The cathode discharge of metal ions and the formation of crystals constitute one and the same process.

[19] H. Volmer, Z. Physik. Chem. **102**, 267 (1922).

[20] Grube and Ruess (Z. Electrochem. **27**, 45, 1921) have shown that in copper solutions with a high content of glue the potential is rhythmic, with a cycle of several minutes. They consider that the discharge of the copper and the glue is continuous but that the deposit undergoes a transformation at intervals.

b. Any given ion is discharged at the point at which the lowest discharge potential is required.

c. The discharge potential is a function of (1) the solution pressure of the metal and (2) the "effective" metal ion concentration adjacent to it.

d. The single potential and solution pressure of a metal are the resultant of (1) the "primary single potential," which is defined in terms of the solution pressure of a single unoriented atom, and (2) the "orientation potential," which is a measure of the diminution in solution pressure and corresponding algebraic increase in single potential caused by the arrangement or orientation of the adjacent metal atoms.

e. A higher potential is required to discharge an ion in a position unrelated to those of previously discharged atoms, (that is, to form a nucleus) than upon an existing crystal, and similarly a higher potential is required to discharge an ion upon a small crystal than upon a large crystal.

2. Typical structures of electrodeposits are classified into three major groups, viz:

Group I. All (or practically all) of the initial nuclei continue to grow.

Group II. Only a part of the initial nuclei continue to grow.

Group III. None of the initial nuclei continue to grow.

Numerous varieties exist in each group.

3. The factors which determine the character of the crystals are discussed, and the direction of the change produced by any change in operating conditions is predicted and illustrated.

DISCUSSION.

E. C. Bain[1] (*Communicated*): It is a pleasure to find such a clear and simple theory advanced for the mechanism of electrodeposition, to supplant the maze of hypotheses which the student was forced to penetrate some few years ago. The authors are

[1] Research Metallurgist, Atlas Steel Corp., Dunkirk, N. Y.

to be congratulated upon the classification of plating types found on page 403, and especially upon the concise tabulation of the effects of the variables upon the crystal type production as briefly set forth on page 415.

In connection with the x-ray investigation of the writer, the most important contribution is probably the information that all electrodeposited metals examined were thoroughly crystalline, and that the grain size, that is, the size of particles of uniform orientation, varies over a range quite comparable with that of the ordinary metals solidified from the melt.

In connection with the matter of the first nuclei, it would not appear that there is at hand sufficient information to attempt a comprehensive definition of the nucleus other than the single atom. This information is probably of the statistical nature observed in gaseous ionization, as far as occurrence is concerned. However, it seems likely when a metal is deposited in an adherent plate upon a cathode metal of similar atomic arrangement, and atomic volume, that the orientation of the depositing metal will be determined by the grains below. Those grains which present an orientation unfavorable for grain growth will doubtless soon be "smothered out" by grains more fortunately orientated. Such a situation should arise in plating gold upon clean silver or nickel upon clean copper.

The writer would question the assumption that rolled or burnished cathodes were in effect at all amorphous. The most severely worked and unannealed metal available—probably ever produced to date—showed almost perfect crystallinity to the x-ray crystallometer. Such a material is the finest tungsten filament which is not crystallized during reduction from a diameter of nearly 0.5 in. to a diameter of 0.0005 in.

Tammann in the new edition of "Lehrbuch der Metallographie" has much of interest on the matter of establishment of the nucleus for a crystalline lattice in a fused metal, and it seems now that it might apply to the phenomenon of electrodeposition.

In this same connection, Tammann reports that when two metals are simultaneously deposited the two kinds of atoms form at random in the space-lattice of the metal which acts as solute in the solid solution. If there is a simple ratio in the number of

the two kinds of atoms, such as 1:3, then subsequent heating to the re-crystallizing temperature will cause an atomic place interchange within the grains, resulting in the most even distribution of the atoms possible. This is, of course, the geometrically symmetrical arrangement. The writer has corroborated this view in the case of the gold-copper alloys, and also in case of the electrolytic brass. This material when plated out has the space-lattice type of copper with a slightly different spacing between the atoms.

The writer is much inclined to the rythmic hypothesis of deposition. The areas where deposition is taking place by preference, at the instant, flash from one facet to another over the surface of the cathode, returning to the first after a sufficient concentration of the metal ion is reached in the electrolyte adjacent by diffusion. This would account for the view long held that the atoms are laid down in rather extensive layers.

C. P. MADSEN[2]: In our research on nickel we found that in considering the microstructure, with relation to a theory of crystallization, that nickel must be considered as a special case. I doubt whether generalities applying to other metals will apply to nickel. There are two reasons: To begin with, it is possible to deposit two entirely different types of nickel metal. Unfortunately authors do not always disclose which type is being deposited. It may be either the absolutely pure nickel, or more usually the hydride of nickel. Most nickel of the old plating art is the hydride form.

The physical properties and characteristics of behavior of the hydride of nickel or the hydride of nickel and iron are totally different from that of the pure metal. The hydride always contracts during deposition. Its crystal structure may be influenced usually more by that of the base metal, while on the other hand the pure nickel can be deposited without any contraction whatsoever, and it has peculiar properties even different from those of pure rolled nickel. In order to determine what made a deposit stick and what prevented it from sticking, we made a lot of microphotographs and we found that some of that work agrees with Dr. Blum's theory, but it also showed that there are several other factors not considered by Dr. Blum.

[2] Consulting Engineer, New York City.

We take a sheet of Bessemer steel with its crystals more or less distorted by cold work. Now we clean that sheet and deposit upon it the nickel hydride. The tendency of the hydride is to form a small plate on the face of each crystal leaving appreciable gaps or spaces at the crystal boundaries between the plates.

These plates represent a thickness of about 0.0002 in. Now we go 0.0001 in. more and apparently there is a sharp change; 0.0002 in. happens to be about the thickness of commercial nickel plating, and we found that as that thickness is exceeded, a distinct change in the structure occurs. The gaps between the small plates will bridge over and then, instead of each individual plate contracting, the whole face of the sheet contracts as a unit, and in doing so the plate cracks at many places, forming open spaces. If you plate to about 0.0005 in. in thickness, the whole plate will peel and drop off the face of the steel, no matter how clean the steel was to start. Of course, in Bessemer plate which has been pickled, the line surface will not be a straight line. It will be highly irregular. If now the nickel film adheres mechanically to some of those irregular points, a strain will be set up and the plate will snap off.

If the hydride is deposited, the micro-structure will be incomplete and difficult to define. When the pure metal is deposited, the same primary phenomenon takes place, with the exception that the spaces between the small plates on the individual crystal faces are exceedingly small; in fact so small that it is difficult to discern any space at all. As the deposit is thickened to about 0.0003 in. it changes over to a fibroid structure. We will have to go to higher magnifications to determine the facts more accurately. There is now available a micro outfit that goes up to 25,000 diameters. I hope to be able to show at the next meeting some of these things much more definitely.

F. C. MATHERS[3]: This is a very important paper and I think it is a valuable starting place for developing a real scientific basis of electrodeposition. However, there are some other facts that will have to be put into the theory. I do not believe that enough importance has been given to the effect of colloids.

In a great many cases the most important influence on the

[3] Univ. of Indiana, Bloomington, Ind.

deposit is produced by these addition agents or by these colloids. Take a solution of silver nitrate, for instance; the deposit from that solution is crystalline and looks just as shown by the photograph in Dr. Blum's paper. If tartaric acid or metaphosphoric acid is added to the silver nitrate solution, the deposit is hard and firm. Now there is very little difference between these solutions. There is some change probably in the conductivity, but no change in the concentration of silver. There may have been some change in the so-called available silver ion. Nevertheless, there are things in connection with that solution that must be explained.

Then we must take into account the effect of the acid ion in the plating bath. In a solution of lead perchlorate, glue is not a good addition agent in preventing crystalline structure. With lead fluosilicate, glue is a good addition agent. Now we cannot say, from any theory presented here, why glue has different effects in these two lead baths. There must be some theory to account for this.

The so-called poisons have the opposite effect of these beneficial colloids. If one takes a lead fluosilicate solution and introduces small quantities of an iodide, the deposit changes to a loose, black, spongy mass and the bath is practically ruined. I could name many other poisons which act in a similar way.

In a general way, I am inclined to believe that in these metal baths we are really depositing a complex on the cathode, and that this complex is made up of the metal in question, of the colloid and probably often of the other ions that are present in the bath. I do not see how to prove that, but to me the evidence indicates it.

LOUIS KAHLENBERG[4]: It is well known that from silver nitrate solutions in water loose crystalline deposits are obtained, whereas from potassium silver cyanide solutions dense deposits, that may be burnished, result. Some have explained this by saying that in the nitrate solution there is an abundance of silver ions, and that in the cyanide solution the concentation of silver ions is small. However, if you take a dilute solution of silver nitrate (make it as dilute as you like and rush plenty of it through the electrolytic cell) you will always get crystalline deposit and never one

[4] Professor of Chemistry, Univ. of Wisconsin, Madison, Wis.

that can be burnished. On the other hand, from the cyanide solution the loose crystalline deposit does not form. Again, from silver nitrate in pyridine a loose deposit does not form, the plating being much like that from the cyanide solution. Thus it is perfectly clear that the nature of the electrolyte is of fundamental importance, and that it is not merely a question of the concentration of the silver ions as deduced from potential measurements.

WM. BLUM: On page 415 of our paper we state "The effect of one or more changes in operating conditions is determined by the resultant of their influences upon the potential relations." A study of silver nitrate solution containing tartaric acid, or of the double silver cyanide solution, will certainly show that a higher potential is required to deposit silver from such solutions than from the nitrate. The theory which we have suggested, does not necessarily require that such a change in potential is a measure of the change in metal ion concentration, although we have employed that assumption as a working hypothesis.

CARL HERING[5]: Some chemists speak with hesitancy about "solid" hydrogen. I do not see why they should hesitate because, in the similar case of oxygen, I think that it is quite proper to say that oxygen is a solid in all metallic oxides. Much to the discomfiture of some professors, I claim that when oxygen of the air combines with a metal forming a solid oxide, there is set free the latent heat of vaporization and solidification of the oxygen. If there are any solid hydrides, I do not see why hydrogen should not be considered a solid in that compound.

W. G. HARVEY[6]: I suppose there is a similarity in the plating out of a metal in aqueous solution to the same phenomenon in fused salts, although it is difficult to draw exact conclusions. There is definite reason to believe that in the electrolysis of fused salts we often have the metal plating out at a finite distance from the cathode. Occasionally when a fused electrolyte is explored with the voltmeter, one is able to indicate zero voltage before the cathode is actually reached. I have always attributed this to the presence of conducting metallic mists dissolved in the electrolyte.

[5] Consulting Electrical Engineer, Philadelphia, Pa.

[6] Vice-President and Superintendent, American Magnesium Corp., Niagara Falls, New York.

I think that we have a right to say that in fused baths the deposition may take place at some distance from the cathode. This is easily noticed when working with metals having a high vapor pressure.

WM. BLUM: The increased tendency toward the formation of trees when the solution was warmed, was probably due to the decrease in resistivity of the solution and the consequent increase in current density produced by the constant voltage. We would predict that if the current density had been maintained constant, there would be a decreased tendency toward treeing at the higher temperature.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

SOME RELATIONS BETWEEN THE MICROSTRUCTURE OF METAL SURFACES AND ELECTRODEPOSITS MADE THEREON.[1]

By A. Kenneth Graham.[2]

Abstract.

This paper presents further evidence of the influence of the structure of the base metal on electrodeposits. A distinction is made between primary influence or true reproduction and secondary influence or the effect of this reproduction on the deposit at large. Where reproduction is obtained large crystals in the base metal produce the most marked secondary influence on the electrodeposit. Reproduction of the structure of both copper and brass base metal, but not of nickel, was obtained in copper deposits. Results obtained with nickel deposits on both copper and nickel base metal are uncertain, owing to the difficulty experienced in attempting to reveal their structure upon etching.

The first study of electrodeposits to reveal any influence of the base metal on the structure of the deposit was made by Blum and Rawdon.[3] At the time of presentation of their paper Geo. B. Hogaboom referred to one case in his experience where the structure of silver deposits was affected by the steel base metal. The writer also made a few remarks at that time supporting Dr. Blum's findings, and suggested that a distinction be made in the use of the terms reproduction and influence as applied to the base metal and electrodeposit.

The term reproduction should refer to cases where new crystal

[1] Manuscript received June 18, 1923.

[2] The John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, Pa.

[3] Trans. Am. Electrochem. Soc. 44, 305 (1923).

a

x 130 $H_2O_2 . NH_4OH$

b

x 130 $H_2O_2 . NH_4OH$

FIG. 1.

Copper deposit on cold worked copper sheet showing reproduction of base metal structure in the deposit. (a) Plated at 3 amp per sq. dm. (b) Plated at 1 amp. per sq. dm. and deeply etched.

a

x 500 $H_2O_2 . NH_4OH$

b

x 130 $H_2O_2 . NH_4OH$

FIG. 2.

Copper deposit on cold drawn copper rod at 1 amp. per sq. dm. (a) Showing absolute reproduction of base metal structure in the deposit. (b) Showing structure of the resulting deposit.

growth does not begin, and where the structure at the surface of the base metal is continued in the deposit. The influence of the base metal is also noticeable in its effect on the structure of the electrodeposit, as a result of reproduction, after the deposit has become thick enough to assume its characteristic electrolytic structure. The former might well be called the primary influence and the latter the secondary influence.

The following is the experimental work on which the writer based his remarks, but which was not completed soon enough to permit publishing at that time.

PROCEDURE.

All cathodes were cleaned with a preparatory alkaline cleaner and then in an acid bright dip of the composition given below. Just before plating they were dipped in a cyanide solution containing approximately 2 oz./gal. (15 g./L.) and then rinsed in water. They were then plated in the following copper sulfate solution; in all cases where the preliminary treatment was varied mention will be made of it.

Bright Dip Solution.

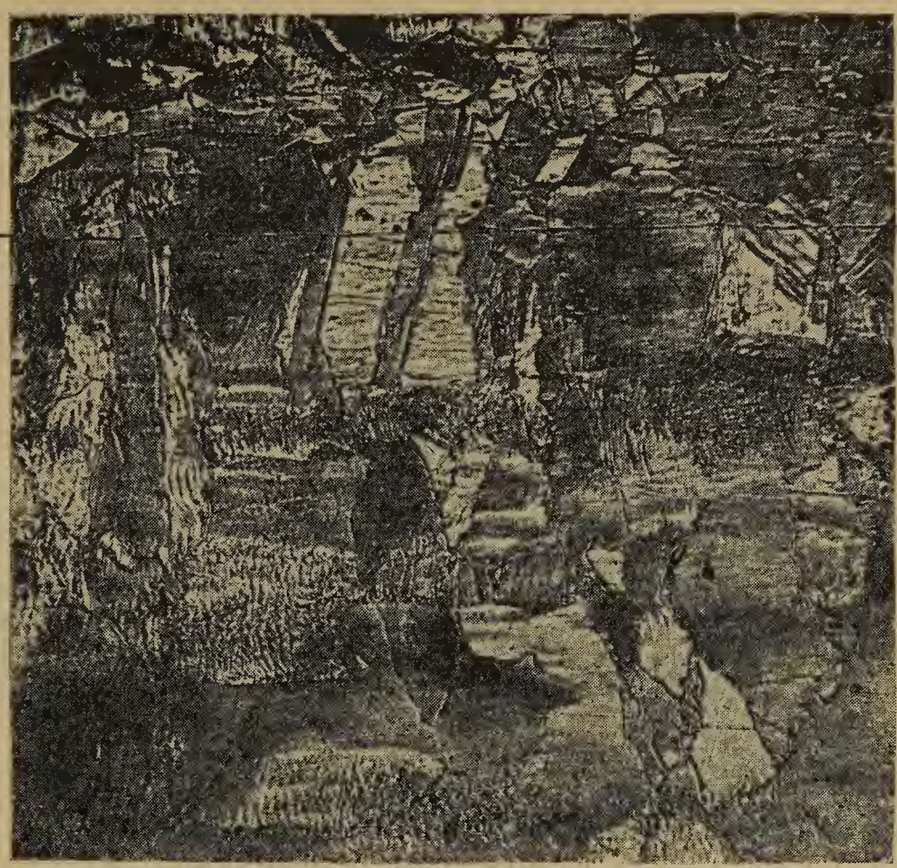
Solution		Sp. Gr.	Volume	Normality
H_2SO_4	66°	1.84	1.00	17.7
HNO_3	40°	1.38	1.00	6.75
HCl	21°	1.17	0.02	0.32

Copper Plating Solution.

Solution	g./L.	Normal
$CuSO_4 \cdot 5H_2O$	188	1.50
H_2SO_4 66°	49	1.00

Considerable difficulty was experienced in etching some of the deposits. This was particularly so where the crystals were large. Since the etching attack in most cases is heaviest at the grain boundaries, and frequently starts there on first immersing in the etching reagent, the fewer grain boundaries especially in large grained electrodeposits gave rise to peculiar etching effects. In some cases the true structure was not clearly revealed, owing particularly to deep etching pits. Most satisfactory results were

a



x 130 $H_2O_2 . NH_4OH$

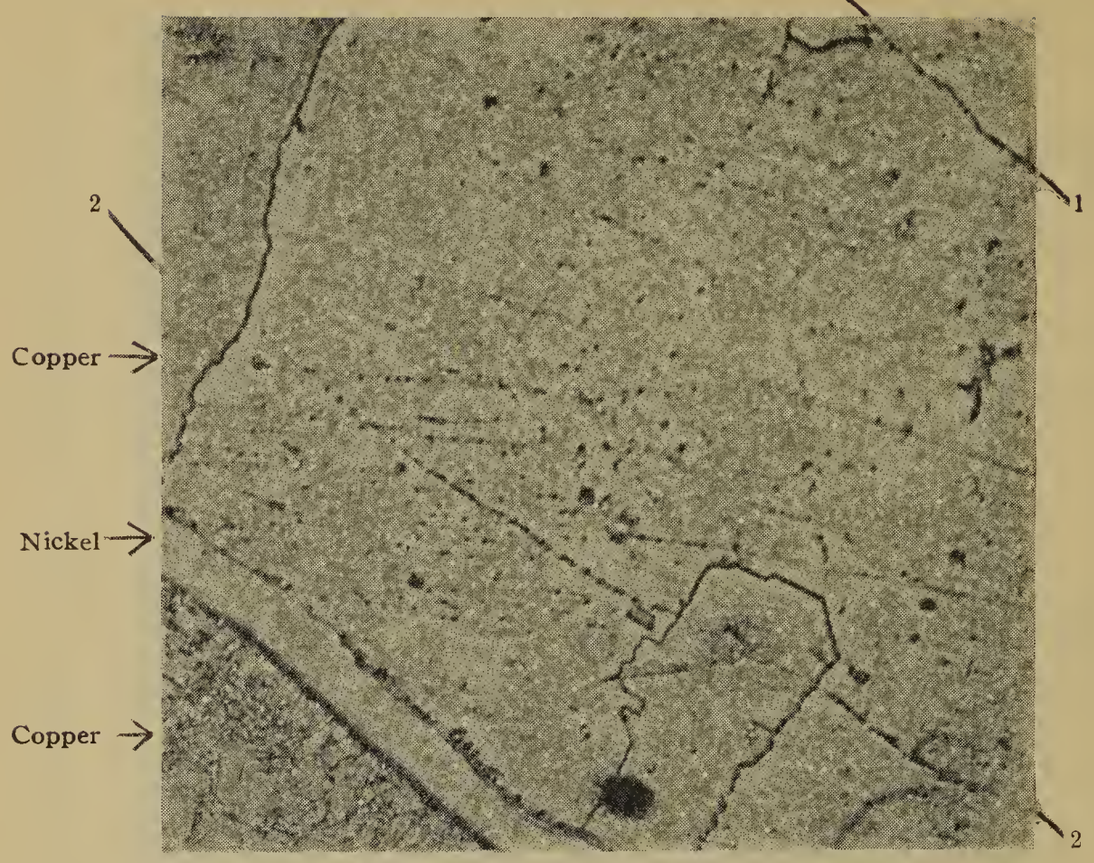
b

x 130 $H_2O_2 . NH_4OH$

FIG. 3.

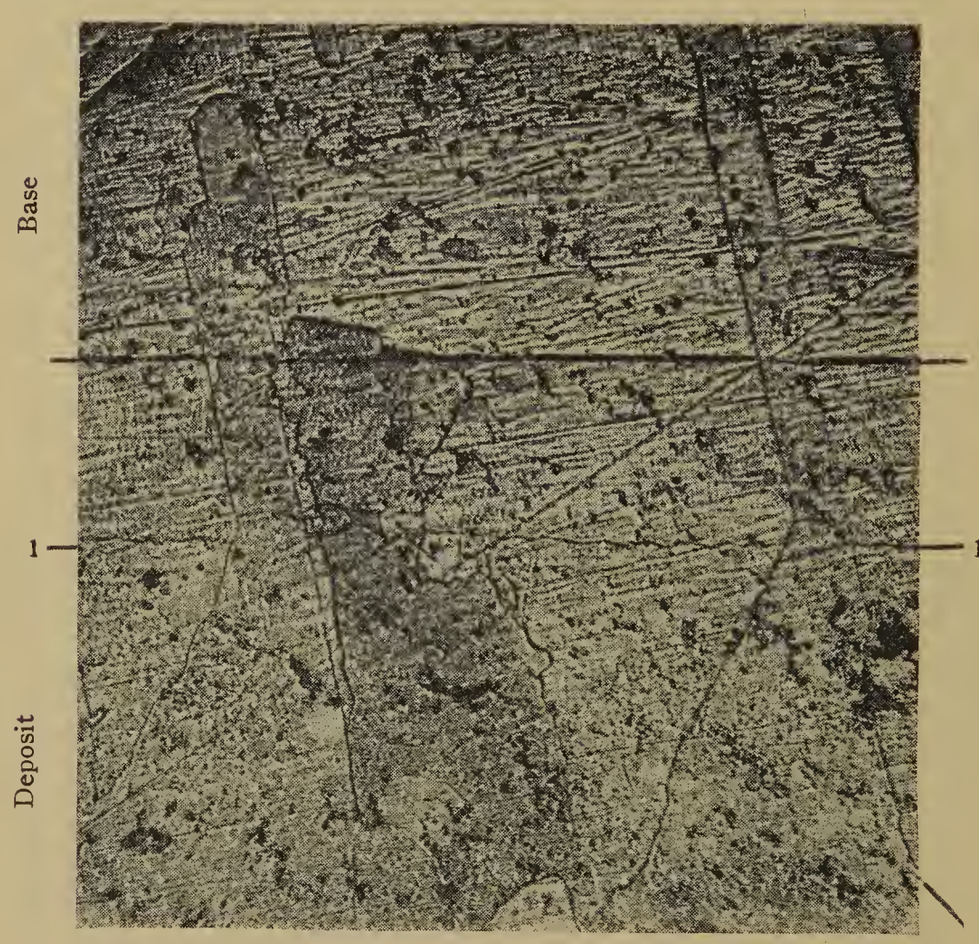
Copper deposit on annealed copper sheet. Current 1 amp. per sq. dm. (a) Showing reproduction of large grains. (b) Showing large grained structure of the deposit. Both deeply etched.

a



x 500 $H_2O_2 . NH_4OH$

b



x 130 $H_2O_2 . NH_4OH$

FIG. 4.

(a) Showing portion of large electrolytic crystal with current interruptions at 1 and 2 for cyanide and acid dips respectively, but continued growth. New crystal growth of copper after nickel plating. (b) Copper deposit with current interruption at 1—1 for water rinse, but no new growth. Current—1 amp. per sq. dm.

obtained on copper by first etching lightly with dichromate and concentrated sulfuric acid to reveal the structure, and then with hydrogen peroxide and ammonium hydroxide to produce contrast.

EXPERIMENTAL RESULTS.

On Cold Worked Copper Sheet.

Two samples of cold worked copper sheet 0.476 cm. (3/16 in.) thick were cleaned and plated at 1 and 3 amp. per sq. dm. (9.1 and 27.3 amp. per sq. ft.). Both illustrations in Fig. 1 show reproduction of the base metal structure in the deposit. The depth of penetration of the primary influence is about the same in each case. The current density did not seem to influence it, and the apparent difference in structure of the columnar deposit below is due to etching.

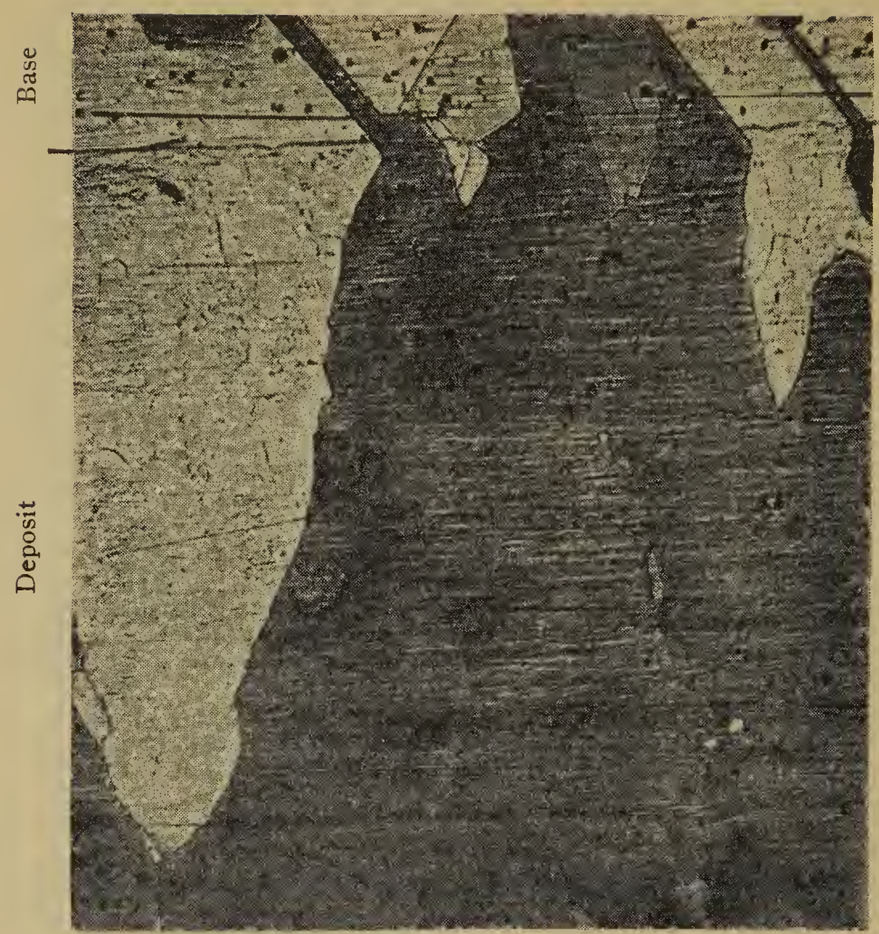
On Cold Drawn Copper Rod.

A piece of 0.63 cm. (¼ in.) cold drawn copper rod was cleaned as described above, but after being exposed to the laboratory atmosphere for about a month acquired a heavy tarnish. After scouring with pumice and an alkali cleaner it was dipped in cyanide and water and then copper plated at 1 amp. per sq. dm. (9.1 amp. per sq. ft.). Fig. 2 (a) shows complete reproduction. Illustration (b) shows the fine grained deposit at a lower magnification.

On Annealed Copper Sheet.

Two pieces of 0.476 cm. (3/16 in.) copper sheet were held in an annealing furnace for 5 hr. at 775° C. and then allowed to cool in the furnace. The heavy oxide coating was removed with hot 10 per cent sulfuric acid and dichromate dip. They were then given a bright dip and treated in the usual manner with cyanide before plating. The first was plated at 1 amp. per sq. dm. (9.1 amp. per sq. ft.) and after several hours was removed from the solution, rinsed several times in water and then returned to the plating solution. This was done to observe what effect the interruption would have on the deposit. In Fig. 4 (b) the line 1 in the deposit caused by this interruption may be clearly seen, but the

a



x 130 $H_2O_2 . NH_4OH$

b

x 130 $H_2O_2 . NH_4OH$

FIG. 5.

Copper deposit on annealed copper sheet revealing same orientation in deposit on etching. Current 3 amp. per sq. dm. (a) Showing large structure of same orientation but resistant to etching. (b) Showing reproduction. Deeply etched.

a

x 500 $H_2O_2 . NH_4OH$

b

x 130 $H_2O_2 . NH_4OH$

FIG. 6.

Copper deposit on buffed cold worked copper sheet. (a) Cleaned in alkali and cyanide only before plating. Line 1—1 shows same growth after interruption. (b) Bright dipped and dipped in cyanide before plating, showing reproduction of base metal surface in deposit. Current—1 amp. per sq. dm.

etching lines run straight through it showing a continuation of the former structure. Fig. 3 (a) shows the reproduction of the large base metal crystals in the deposit. The structure of the deposit itself is obscured by too deep etching. Illustration (b), however, shows the large grained structure of the deposit.

The second piece of annealed copper sheet was copper plated at 3 amp. per sq. dm. (27.3 amp. per sq. ft.) for 18 hr., and then removed from the plating bath long enough to dip in cyanide and rinse in water. It was then returned and the deposition continued. After several hours it was removed, given an acid bright dip, rinsed in water and again returned to the plating bath. Finally it was removed, given a bright dip, nickel plated and again copper plated. The result of all these interruptions is shown in Fig. 4 (a), which is a picture at high magnification near the edge of a large electrolytic crystal. The first two interruptions represented by lines 1 and 2 show no change in the crystal structure of the deposit. The nickel deposit which was the third interruption did not etch, but the copper which followed started a complete new crystal growth.

The first picture (a) of Fig. 5 resisted the etching attack, so that the grain structure is not fully revealed. The second (b) is more deeply attacked, but the action has been one of pitting rather than an attack of the grain boundaries. This behavior seemed characteristic of the large grained deposits on the annealed samples. The orientation of the crystals of the base metal and the deposit are the same, however, the etching characters continuing straight through both at the line of deposition.

On Buffed Copper Sheet.

Fig. 6 (a) shows the structure of copper deposited at 1 amp. per sq. dm. (9.1 amp. per sq. ft.) on a buffed copper surface which was previously cleaned in alkali cleaner and cyanide only. The deposit appears to be a new crystal growth. The writer is inclined to regard it not as a new crystal growth, however, but as a reproduction of the small grained, greatly deformed, buffed surface. This opinion is somewhat strengthened by the result obtained in Fig. 6 (b). Here the buffed surface was given a very light bright dip, just sufficient to remove some of the very small surface

particles, a cyanide dip, water rinse and then copper plated. The resulting deposit shows complete reproduction of the surface, both large and small grains.

On Annealed Brass Sheet.

A sample of 0.3 cm. (0.119 in.) sheet brass was annealed in an electric furnace at 540° C. for three hours and allowed to cool in the furnace. It was then given a sulfuric acid pickle, an acid bright dip and finally a cyanide dip before plating. The sample was then copper plated at 1 amp. per sq. dm. (9.1 amp. per sq. ft.).

Considerable difficulty was experienced in etching this sample as the brass and electrolytic copper had a tendency to etch selectively, in most cases leaving the latter unattacked. If, however, the etching was continued for a longer period the structure of the brass was destroyed and this particularly at the line of deposition. Ammonia and hydrogen peroxide gave only fair results. Fig. 7 (a) shows large grains of copper at the beginning of the line of deposit. The brass structure is too deeply attacked to show exactly what structure is being reproduced at the line of deposition, but it is entirely evident that a new crystal growth has not taken place. Fig. 7 (b) and (c) at higher magnification further confirms this.

On Nickel.

In all cases where deposits of copper were made on nickel electrodeposits a new crystal growth took place. Fig. 4 (a) illustrates this. Nickel deposited on annealed nickel base metal gave results which owing to etching difficulties are very uncertain.

DISCUSSION OF RESULTS.

Reproduction, therefore, does not depend so much on the preliminary chemical treatment as on the state of the metallic surface.

Metal that does not have well formed crystals at the surface, therefore, does not necessarily start a new growth on electroplating, but apparently reproduces the surface crystals whatever they may be. The influence of these small crystals does not penetrate deeply into the electrodeposit, however, so that the columnar structure of the electrolytic metal soon makes its appearance. If

the original base metal crystals are large, their penetration into the deposit is greater, and the final electrolytic structure is not only much larger but differs in etching characteristics from the former case. A comparison of the structure of the deposits in Fig. 6 (a), 2 (b) and 3 (b) where the current density was the same will confirm this. This latter difference in structure, as a

a

x 130

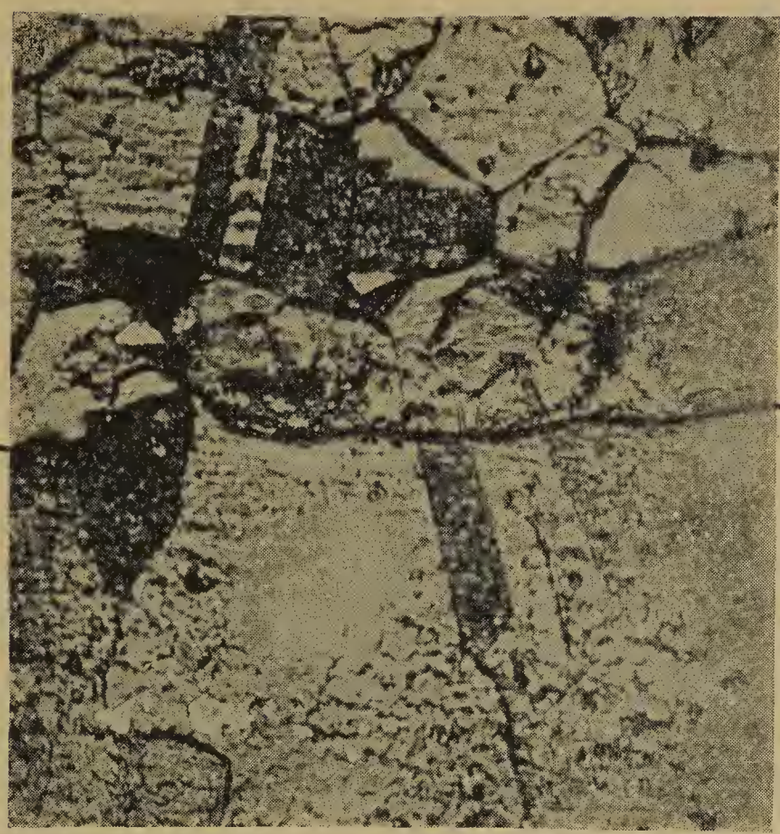
FIG. 7.

Copper deposit on annealed sheet brass at 1 amp. per sq. dm. Etched electrolytically with saturated NH_4Cl solution. (a) Shows large crystals starting at line of deposit. See (b) and (c) on next page.

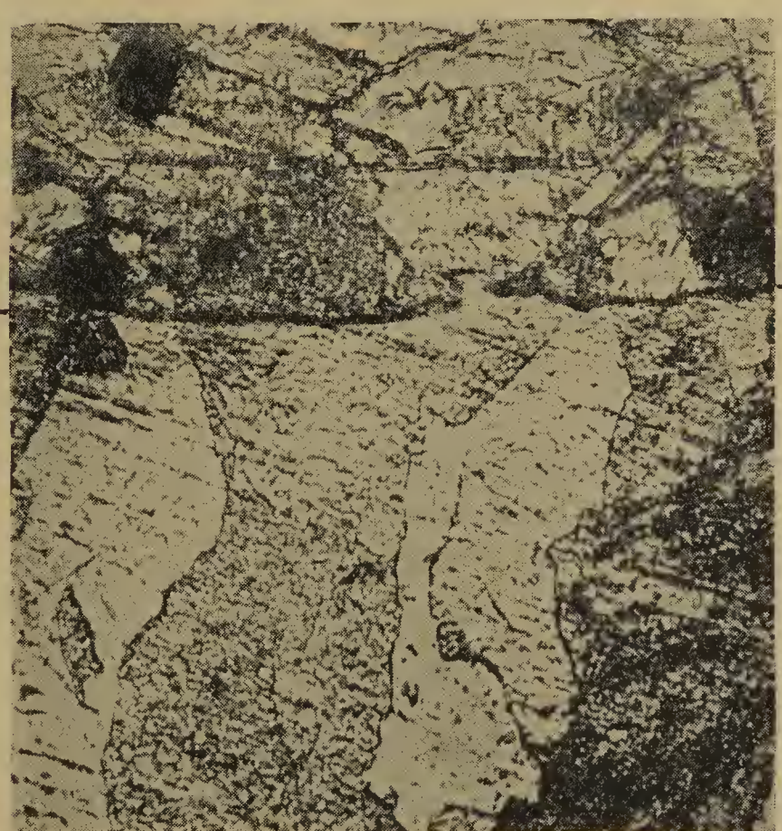
result of the initial influence of the base metal or reproduction, the writer regards as a well-defined secondary influence of the base metal structure on the structure of the electrodeposit.

With such simple evidence of the influence of the base metal on electrodeposits it may appear strange that it was not observed in some of the earlier studies. One probable reason the writer can offer is the difficulty experienced in attempting to reveal the

b



c



x 500

FIG. 7.

Copper deposit on annealed sheet brass at 1 amp. per sq. dm. Etched electrolytically with saturated NH_4Cl solution. (b) and (c) show reproduction. See (a) on opposite page.

true structure of the deposits, particularly at the line of deposition. An entirely false impression of the crystal structure of the deposit is often obtained. This is especially so in the case of nickel, and where the base metal and deposit are of different metals. Then too, the etching attack is usually heaviest at the line of deposition, which also destroys all possibility of observing reproduction.

DISCUSSION.*

WM. BLUM[1]: Such a distinction as Mr. Graham has made may be useful, even though it is not sharply defined. The general principles of crystal growth will probably determine the relation of the structure of any layers to those previously deposited, regardless of whether or not the initial layers owe their structure to that of the underlying base metal.

C. P. MADSEN[2]: I do not agree with Mr. Graham's conclusions because two considerations have not been taken into account. First, he has omitted making deposits on ferrous metals; second, he has omitted nickel.

In his first conclusion he says, "Reproduction, therefore, does not depend so much on the preliminary chemical treatment as on the state of the metallic surface." I think neither is correct. My opinion is that when the work is completed it will sum up something like this: that any electrode deposit tends to copy the structure of any metal. Whether it does so or not depends upon the condition of the metal surface and whether it has been cleaned by chemical or mechanical means.

Furthermore, Mr. Graham is not justified in drawing a conclusion that the reproduction or tendency to reproduce the base metal structure is always undesirable. It may be desirable, for instance, to deposit a copper surface which copies the fine structure of a rolled copper base. On the other hand, it may safely be said that it is always undesirable for a nickel deposit to copy the structure of any metal other than nickel upon which it is deposited,

* In the absence of the author the above paper was presented by Wm. Blum.

[1] Chemist, Bureau of Standards, Washington, D. C.

[2] Consulting Engr., New York City.

because the natural structure of a pure nickel deposit is so fine that its hardness and tensile strength may be even greater than that of the best tool steel obtainable. Therefore, if the strength of electrodeposited metal is a function of the structure, as it is in metals made by melting, it is undesirable that nickel copy the structure of metals which are not as strong and hard as the best nickel structure obtainable electrolytically.

A. KENNETH GRAHAM (*Communicated*): Replying to Mr. Madsen's remarks, deposits of nickel were studied; iron was not. I fail to see what bearing this has on the results stated in the paper.

The statement that "Reproduction does not depend so much on the preliminary chemical treatment as on the state of the metallic surface" is not an attempt to explain the mechanism of the observed phenomena. It is merely a contradiction of a statement made in a previous article[3] to the effect that reproduction was obtained if the cathode (copper) were taken from a nitric acid dip into the plating bath, but not if taken directly from an alkaline (cleaning) solution.

Regarding the last statement, I am unaware of making any statement to the effect that reproduction is undesirable. On the contrary, I would be tempted to believe that reproduction would cause greater adhesion of the deposit, with resultant advantages in cases of wear and friction, etc.

[3] The Influence of the Base Metal on the Structure of Electrodeposits. By W. Blum and H. S. Rawdon. See this volume, page 305.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

THE EFFECT OF TEMPERATURE ON OVERVOLTAGE.[1]

By M. Knobel[2] and D. B. Joy.[2]

Abstract.

The hydrogen overvoltage on cathodes of smooth and platinized platinum, silver, copper, nickel and lead were measured at various temperatures from 0 to 75° C. The method employed for making the measurements was found to give fairly reproducible results. In almost every case the overvoltage decreases directly as the temperature of the electrolyte increases. The electromotive force of the cell H_2 , $2N$ H_2SO_4 , Hg_2SO_4 , Hg was measured at temperatures from 0 to 90°.

The existing data[3] on the effect of temperature on overvoltage are in many cases quite unreliable, and the experiments are made with too few electrodes to allow generalizations. The most important criticism is that insufficient care has been taken to exclude any possible variations of the electrode and its overvoltage with time. It is well known[4] that the overvoltage will not remain constant for more than a few minutes even if the temperature and current density, etc., are kept perfectly constant. Probably the best work is that of Tafel,[5] but he used only a mercury cathode and one cannot be sure that there was not a systematic change in his electrode while going from one temperature to the next. In

[1] Manuscript received June 11, 1923.

[2] Rogers Lab. of Physics, Electrochemical Lab., Mass. Inst. of Tech., Cambridge, Mass.

[3] Coehn and Neumann Z. phys. Chem. **39**, 353 (1902); Kaufler, Z. Elektrochem. **13**, 633 (1907); Tafel, Z. phys. Chem. **50**, 672 (1904); Pring and Curzon Trans. Far. Soc. **7**, 237 (1912); Roszkowski Z. pyhs. Chem. **15**, 267 (1894); Sacerdotti Z. Elektrochem. **17**, 473 (1911); Rideal, J. Am. Chem. Soc. **42**, 94 (1920).

[4] c. f. Lewis and Jackson Proc. Am. Acad. **41**, 399 (1906).

[5] *loc. cit.*

the present research we have been successful in eliminating the effect of erratic changes in the overvoltage with time, and have obtained fairly reproducible measurements.

PROCEDURE.

Several preliminary methods of making measurements were unsuccessful, but will be mentioned briefly as they illustrate the probable errors in previous work. The first method attempted was to obtain the complete overvoltage-current density curves at intervals of ten degrees from 0 up to 90°. It was found, however, that on returning to the original temperature (0°) the overvoltages were so different from their original values at the start of the run that it would be out of the question to compare the 90° values with those taken at 0°. Such a run might last 3 to 4 hr. in which time the plated electrode usually became noticeably roughened and had then a lower overvoltage.

The second method was to maintain the current density constant and to raise and lower the temperature, meanwhile measuring the overvoltage. The temperature could be changed from 0° to 90° and back in possibly 1 hr. including pauses of 2 to 3 min. at each ten degrees, but even in this time the overvoltage was always different on the return to the low temperature from what it had been at the start. A preliminary polarization for two days at the stipulated current density would still not result in constant values.

Finally, to increase the speed with which the electrode could be taken from a low to a high temperature and back, four separate thermostats were set up, each containing a cell with electrolyte, a reference electrode, anode, etc., and maintained at approximately 0°, 20°, 50° and 75° respectively. The electrode was then placed in each cell successively and the overvoltage measured, whereby one could go up and down the given temperature range three to four times in less than one-half hour. In this way, overvoltage values were obtained which checked satisfactorily at each temperature.

It is in the light of these preliminary experiments, where the erratic fluctuations with time were found to be so troublesome,

that we feel justified in questioning the reliability of previous data.

APPARATUS.

The details of the cell, electrodes, and method of measuring the overvoltage were as described in a previous article[6] with the following exceptions. Asphalt could not be used to cover the back of the electrodes at the high temperatures, but instead 1 sq.

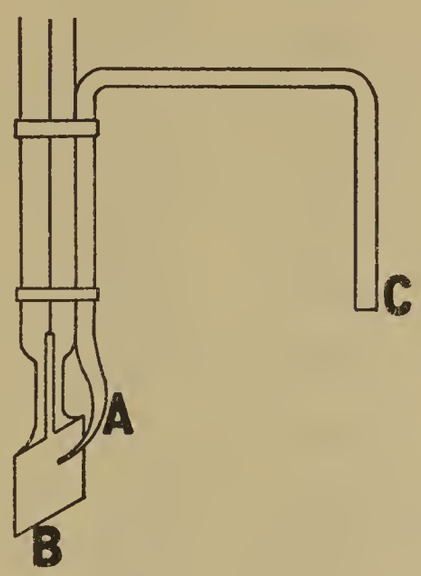


Fig. 1

Table I.

Electromotive force of cell H_2 , H_2SO_4 (2*N*) , Hg_2SO_4 , Hg *at various temperatures.*

Temp. ° C...	2.90	3.25	10.00	20.05	50.04
Volts	0.6784	0.6780	0.6770	0.6750	0.6677
Temp. ° C...	60.00	70.03	79.97	89.95	
Volts	0.6641	0.6601	0.6540	0.6433	

cm. platinum sheets with their leads were coated with lead glass except for the front face. The various metals were then plated on the platinum to a depth of approximately 0.5 mm. Only hydrogen overvoltages were measured, and for these the electrolyte was 2*N* H_2SO_4 with a mercurous sulfate reference electrode. The reference electrode could not be carried from one thermostat to

[6] Knobel, Caplan and Eiseman, Trans. Am. Electrochem. Soc. 43, 55 (1923).

TABLE II.

Hydrogen Overvoltages at Various Temperatures.

	Silver, 40 amp./sq. dm.			
Temp. ° C.	0.33	21.4	47.6	73.4
Volts	0.760	0.717	0.672	0.618
	0.758	0.716	0.689	....
	....	0.716	0.667	0.619
	0.757	0.715	0.669	....
	....	0.711	0.665	0.608
	0.756	0.713	0.666	....
	Silver, 10 amp./sq. dm.			
Temp. ° C.	0.3	21.4	47.5	73.5
Volts	0.657	0.574	0.521	0.495
	0.674	0.620	0.552	....
	....	0.615	0.551	0.496
	0.672	0.614	0.552	....
	....	0.613	0.553	0.494
	0.675	0.613	0.552	....
	Silver, 1 amp./sq. dm.			
Temp. ° C.	0.4	21.5	47.5	73.5
Volts	0.412	0.362	0.300	0.242
	0.421	0.366	0.302	....
	....	0.369	0.303	0.242
	0.423	0.365	0.302	....
	Copper, 40 amp./sq. dm.			
Temp. ° C.	0.4	20.0	47.4	73.5
Volts	0.572	0.508	0.456	0.395
	Copper, 10 amp./sq. dm.			
Temp. ° C.	0.4	20.1	47.2	73.2
Volts	0.486	0.429	0.371	0.300
	Copper, 1 amp./sq. dm.			
Temp. ° C.	0.4	20.2	47.4	73.9
Volts	0.347	0.275	0.196	0.139
	Nickel, 10 amp./sq. dm.			
Temp. ° C.	0.3	21.6	47.8	73.5
Volts	0.682	0.635	0.572	0.505
	Nickel, 1 amp./sq. dm.			
Temp. ° C.	0.4	21.6	47.8	73.0
Volts	0.491	0.420	0.359	0.295

TABLE II—*Continued.*

	Lead, 40 amp./sq. dm.			
Temp. ° C.	0.4	22.6	46.2	72.2
Volts	1.151	1.128	1.092	1.042
	Lead, 10 amp./sq. dm.			
Temp. ° C.	0.4	22.6	46.2	72.2
Volts	1.146	1.110	1.062	1.001
	Lead, 5 amp./sq. dm.			
Temp. ° C.	0.5	22.6	46.9	72.0
Volts	1.040	1.002	0.996	0.926
	Lead, 0.5 amp./sq. dm.			
Temp. ° C.	0.3	21.4	43.8	72.0
Volts	0.850	0.771	0.670	0.41
	Lead, 0.1 amp./sq. dm.			
Temp. ° C.	0.3	21.4	44.8	72.5
Volts	0.550	0.412	0.320	0.319
	Smooth Platinum, 0.5 amp./sq. dm.			
Temp. ° C.	0.2	22.2	47.5	73.0
Volts	0.60	0.51	0.44	0.41
	Platinized Platinum, 40 amp./sq. dm.			
Temp. ° C.	0.3	19.0	47.0	74.0
Volts	0.061	0.061	0.061	0.061
	Platinized Platinum, 10 amp./sq. dm.			
Temp. ° C.	0.3	19.20	46.9	74.3
Volts	0.054	0.054	0.053	0.052
	Platinized Platinum, 1 amp./sq dm.			
Temp. ° C.	0.4	19.2	46.8	74.8
Volts	0.039	0.038	0.037	0.036

the next, since considerable time would have been necessary to allow it to come to temperature equilibrium. On the other hand, unless the reference electrode tip were placed at the same point of the cathode surface, small variations in the overvoltage, due to variations in the surface, resulted. The device shown in Fig. 1 was therefore used, a capillary tip A being securely fastened

against the electrode face B, and the device as a unit moved from one thermostat to the next. Connection was made at C to the reference electrode.

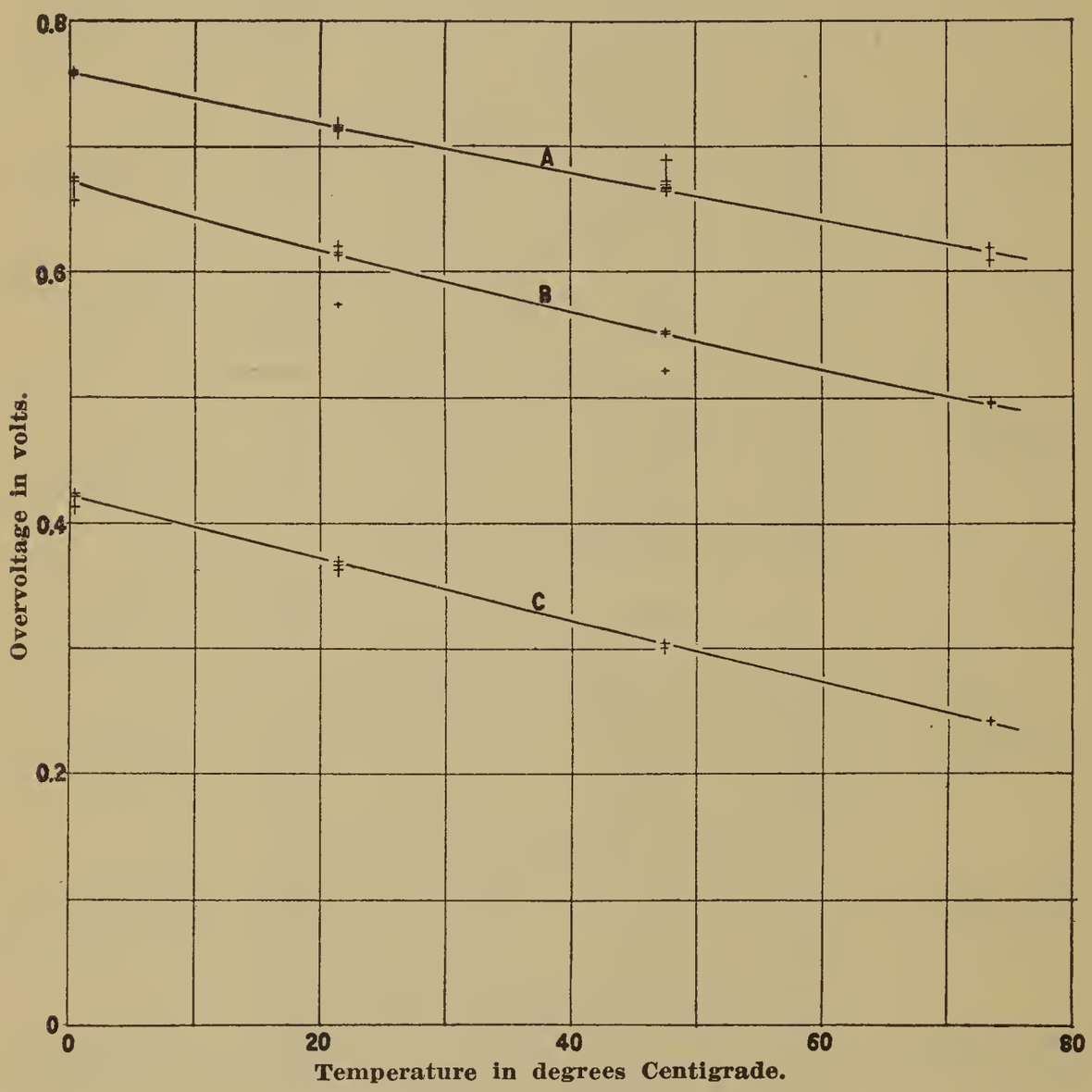


FIG. 2

Change of overvoltage with temperature on silver. A, 40 amp./sq. dm; B, 10 amp./sq. dm.; C, 1 amp./sq. dm.

Temperature Coefficient of Mercurous Sulfate, Hydrogen Cell. It is necessary to know the e. m. f. of the cell H_2 , H_2SO_4 ($2N$), Hg_2SO_4 , Hg at each temperature used, in order to calculate the overvoltage[7]. We were unable to find all the data needed in the literature and therefore made direct determinations. Two carefully prepared mercurous sulfate electrodes which agreed between

[7] Apparently several of the previous investigators mentioned have neglected this point.

themselves within 0.05 m. v. were used, with two platinized platinum hydrogen electrodes whose electromotive forces never differed by more than 0.1 m. v. The measured electromotive forces of the cell at various temperatures are tabulated in Table I. When these data are plotted on a large scale, they lie well on a smooth curve. The average deviation of each electromotive force is estimated to be ± 0.1 m. v. The temperatures are reliable to ± 0.05°.

RESULTS.

The results of the measurements of overvoltage with change in temperature are listed in Table II. The values were determined for two or more different current densities in each case. For the first electrode, in the table, silver, more or less complete data are given to show the degree of reproducibility obtained. The time order of the measurements is obtained by reading from left to right across the first line and then back from right to left on the second line, etc. That is, the electrode was taken progressively up and down through the temperature range. These data are shown graphically in Fig. 2.

It often happened that the first few cycles would give erratic values, but these soon disappeared and the overvoltage values would fall fairly well on one smooth line without any evidence of hysteresis. In the case of all electrodes other than silver, only one overvoltage value at each temperature and current density is given, which is a point taken from the best smooth curve passing through all the points. The departure of any one determination from the smooth line is in general less than 5 m. v. The values for lead and smooth platinum are appreciably less reproducible than the others, particularly at the low current densities. On platinized platinum the deviations seldom exceed 1 m. v.

DISCUSSION OF RESULTS.

In almost every case the curve of overvoltage against temperature is nearly a straight line. The exceptions are smooth platinum, and lead at a current density of 0.1 amp./sq. dm., where the curves are convex toward the temperature axis; and lead at 0.5 amp./sq. dm., where the curve is concave toward the temperature axis. Where the curves are straight lines, or nearly so, an

average slope for the entire temperature range has been calculated with the results listed in Table III.

It is seen that the decrease of overvoltage with temperature is not greatly different on the various electrodes, with the exception of platinized platinum. There appears to be a tendency for the slope[8] to become larger at the lower current densities, but no

TABLE III.

Electrode	c. d. amp./sq. dm.	dE/dT m. v./° C.
Silver	40	2.0
	10	2.4
	1	2.5
Copper	40	2.4
	10	2.6
	1	3.1
Nickel	10	2.4
	1	2.6
Lead	40	1.8
	10	2.0
	5	1.6

relation is apparent between the slope and the magnitude of the overvoltage. In the case of platinized platinum, the overvoltage is practically independent of the temperature between 0 and 75° C.

We are not prepared at the present time to discuss these results from a theoretical standpoint, but hope to do so soon.

DISCUSSION.

COLIN G. FINK[1]: It seems to me that the general slope of those curves in Fig. 2 might have a direct bearing on whether we are dealing with a hydride or merely with occluded hydrogen. The higher the temperature, the more hydrogen is evolved.

[8] It is believed that the slope is the important feature of these data, and not the actual magnitude of the overvoltage. A newly prepared electrode may exhibit consistently higher or lower overvoltages than another of the same metal, but will yield nearly the same value of dE/dT.

[1] Head, Div. of Electrochemistry, Columbia Univ., New York City.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

CHROMIUM PLATING STEEL USING CHROMIUM ANODES.[1]

By Kevie W. Schwartz.[2]

Abstract.

The various solutions suggested in the past for electrodeposition of chromium were investigated, and it was found that Sargent's solution of chromic acid and sulfate gives consistently good results. Hard, bright, adherent deposits on steel were obtained. However, no chromium plate was obtained unless hydrogen in considerable excess was simultaneously discharged at the cathode. Chromium metal anodes were used, and no passivity was observed even after many hours operation. Chrome-plated steel resists the corrosive action of air saturated with ammonia fumes, nitric acid or sulfuretted hydrogen. Chrome-plated steel is not attacked by molten tin, zinc or brass.

Chromium is a bluish-white metal with a specific gravity when crystalline of 6.92 at 20° C. It is exceedingly hard and can be drilled only with great care and difficulty. It holds its bright, silver-like luster almost indefinitely. Samples which were exposed to laboratory fumes for many months did not show any signs of tarnish or corrosion.

Chromium metal occurs in both an active and a passive state. In this respect it resembles iron, nickel and cobalt. When active the metal dissolves readily in hydrochloric and hot sulfuric acids to give chromous salt. Hittorf[3] states that in the presence of most strong oxidizing agents such as free chlorine, bromine, strong nitric acid, *chromic acid,* etc., chromium becomes passive.

[1] Manuscript received May 24, 1923. Abstract of thesis presented in partial fulfillment of the requirements for the degree of Chemical Engineer at Columbia University.

[2] Columbia University, New York City.

[3] Z. Phys. Chem. 30, 505, (1899).

This probably accounts for the fact that chromium anodes have not been used heretofore in depositing the metal from chromic acid solutions. Chromium metal can be immediately activated by making it cathode in an acid solution; by contact with concentrated acids at room temperature by immersion in solutions of the chlorides of the alkalies or alkaline earths at temperatures near their boiling points.

According to Carveth electrolytic chromium may occlude as much as 250 times its volume of hydrogen.

The theoretical ampere hour yield of the pure metal from a valence of three is 0.6458 g., and from a valence of six it is 0.3229 g.

Chromium has at least three different valences. The single potentials according to Luther[4], assuming 0.56 volt for the Ostwald calomel electrode, are 0.3 v. for chromium against its divalent salts, 0.2 v. against its trivalent salts, and 0.9 v. against its hexavalent salts.

Chromic oxide belongs to a class of oxides including those of V, U, Ti and Mn, which are not readily reduced to the metal. Chromic oxide is not reduced by hydrogen or CO at ordinary pressures. It is not acted upon by chlorine or sulfur fumes. Exposed to water or weak electrolytes it hydrolyzes extremely slowly as compared with oxides of most other heavy metals. Chromic oxide forms a very adherent film on the chromium metal or chromium alloy surface. It is largely on account of these valuable properties of the metal and its oxide that we undertook the study of chromium-plating steel.

HISTORICAL.

Bunsen[5] produced metallic chromium electrolytically by using a two-compartment cell and the chloride as electrolyte.

Placet and Bonnet in American patent No. 526,114, Sept. 18, 1894, set forth that the most important compound from which chromium can be obtained commercially is chromic acid. Schick, working under Le Blanc, repeated the work of Placet and Bonnet and obtained mere traces of chromium.

[4] Z. Phys. Chem. **36**, 389, (1900).
[5] Pogg. Ann. **91**, 119, (1854).

Moller and Street (1898) took out patents in England and used as their cathode solution chrome alum, sodium sulfate and water in equal parts by weight. Their current density was 40 amp./sq. dm. and temperature 90° C. Their yield per ampere hour indicates an efficiency of 30 per cent. The patent claims relate mainly to the by-products at the anode and the maintenance of the composition of the solution.

Cowper-Coles (1900) found that a chromic chloride solution 250 g./L. at a temperature of 88° C. and a current density of 40-50 amp./sq. ft. (5 amp./sq. dm.) gave good deposits of chromium, especially when hydrochloric acid was added to redissolve the precipitated oxide.

J. Férée[6] electrolyzed solutions containing 100 g./L. hydrochloric acid and 160 g./L. crystalline chromic chloride with current densities of 15 amp./sq. dm., obtaining, as he claimed, excellent deposits. Using the same current density but a solution containing one gram molecule of chromic chloride to three gram molecules of potassium chloride per liter, he also obtained excellent deposits, with a current efficiency of 45 per cent.

Glaser[7] worked with chromic chloride, sulfate and acetate in the cathode chamber, while the anolyte consisted of mineral acids or salt solutions. He is not definite as to his current densities, temperature, or purity of chemicals used. Hence his results do not bear ready duplication.

Carveth and Mott[8] investigated the electrodeposition of chromium from chloride and sulfate solutions, using a double cell arrangement with lead anodes and copper cathodes. They concluded that chromium can be deposited from these solutions and that the presence of chromous salt appears essential to the successful depositions of the metal from chloride and sulfate solutions. Stirring was found to be undesirable. They recommend as yielding good results a solution containing 340 g./L. chromium sulfate in the catholyte and dilute sulfuric acid (density 1.12) in anolyte, with a current density of 14 amp./sq. dm. (130 amp./sq. ft.) The nature of the anolyte affects the efficiency and deposit materially as does also the temperature used.

[6] Electrometallurgy, p. 366, (1897).
[7] Z. f. Elektrochemie 7, 656 (1901).
[8] J. Phys. Chem. 9, 231.

The article contains a wealth of valuable information and data concerning chromium deposition by use of the electric current.

Carveth and Curry[9] investigated the deposition of chromium from chromic acid solutions. They concluded that a high current density is needed to accomplish this. Their yield of chromium was increased by small additions of a mineral acid.

Le Blanc[10] found he could deposit chromium using a double cell arrangement with lead anodes and copper cathodes, a current density of 15-20 amp./sq. dm. and a catholyte concentration of 89 g./L. of chromium. The anolyte was sulfuric acid of a specific gravity of 1.12 and the temperature used was 38-50° C. Only thin deposits were obtained; thicker deposits showed a tendency to crack and tree.

Salzer[11] prepared a solution of 3 parts green chromic oxide to 4 parts chromic acid (total chromium content of solution 50 to 250 g./L.) He claims a flexible deposit of any thickness. In his later German patent[12] he increases the activity of this bath by using Cr salts such as sulfate or chloride.

Skillman in unpublished work at Cornell, as referred to by G. J. Sargent[13], used a platinum anode, a rotating copper cathode, a temperature of 20° C. and a current density of 100 amp./sq. dm. Best results were obtained from a 150 g./L. chromic acid solution with 20 g./L. sulfuric acid. His yields varied with the electrolysis.

G. J. Sargent[14] examined various mixtures of chromic sulfate and chromic acid and showed that the yield of chromium from chromic acid solutions is greatly increased by the addition of small amounts of chromium sulfate. He obtained good thick deposits on copper, using a platinum anode and a single cell arrangement.

E. Liebreich[15] used a lower voltage with a carefully reduced chromic acid solution. He obtained adherent deposits on iron, copper, nickel and brass. His anodes were of platinum and also of iron; the current density was 10-85 amp./sq. dm. His solu-

[9] Trans. Am. Electrochem. Soc. **7**, 115 (1905).
[10] Trans. Am. Electrochem. Soc. **9**, 315 (1906).
[11] U. S. Patent, 900,597, Oct. 6, 1908.
[12] Ger. Pat. No. 225,769, May 13, 1909.
[13] Trans Am. Electrochem. Soc., **37**, 479 (1920).
[14] *Loc. cit.* p. 479.
[15] Z. f. Metallkunde **14**, 367 (1922), Z. f. Elektrochem. **27**, 94 (1921); Metal Industry **21**, 109 (1923).

tions contained from 100 g./L. to 1,000 g./L. of chromic acid, partially reduced to chromous acid. Without the addition of a little sulfuric acid there was a tendency for the cathode to coat over with a green deposit, presumably Cr_2O_3. The fluctuating voltages he obtained in the chromic acid solutions he attributed "not to passivity," but to alternate reduction and reoxidation of the cathode product. Liebreich is continuing his investigations at the Reichsanstalt, Berlin.

EXPERIMENTAL.

On account of the wide diversity of results and opinions of previous investigators, we decided to study:

1. The effect of chromium sulfate concentration at various current densities.
2. The effect of hydrogen ion concentration.
3. The effect on the deposit upon substituting chromium anodes in place of lead and of platinum anodes.
4. The extent of the passivity of the chromium anodes after prolonged electrolysis.

We also investigated the electrolytic corrosion of the chromium deposit, as compared to other metals and alloys, in such media as concentrated nitric acid, dilute nitric acid, sea water, molten tin, zinc and brass.

APPARATUS AND METHOD.

In the cases where a two-compartment cell was used it consisted of an 800 cc. beaker, into which a porous cup was placed to act as a diaphragm. The outer chamber was filled with dilute sulfuric acid with a specific gravity of 1.12. The anode used was a sheet lead cylinder closely fitted around the porous cup. The cathode was either copper or sheet iron. This arrangement was used only in experiments where the conditions of Carveth and Mott were being duplicated. In all other cases a single cell was used. This consisted of a 600 cc. beaker with two anodes (usually chromium) suspended in the solution, preferably by means of chromium-plated iron wires. The anodes of chromium were prepared by the Goldschmidt process. They were approximately 5 x 3.7 x 3.7 cm. (2 x 1.5 x 1.5 in.) in size.

The chromium sulfate and chromic acid used were Eimer & Amend's "chemically pure grade." All solutions were filtered before using. Cold chromic acid solutions have little or no effect on the filter paper. The iron cathodes were electrolytically cleaned.

DISCUSSION OF RESULTS.

Results of tests made on chromium sulfate solutions varying from 395 g./L. to 80 g./L. and current densities varying from 16 to 2.7 amp./sq. dm. (150 to 25 amp./sq. ft.) were not encouraging. No satisfactory crystalline, adherent plate of chromium on iron was obtained. At the lowest concentration used (80 g./L.), a uniformly distributed deposit of a green oxide of chromium was produced.

With high concentrations of chromium sulfate, 350-400 g./L., at current densities ranging from 2.7 to 16 amp./sq. dm. (25-150 amp./sq. ft), with the hydrogen ion concentration varied by introducing sulfuric acid into the bath in increasing amounts, no satisfactory deposit was obtained. At any given current density, as soon as a definite hydrogen ion concentration was exceeded no deposit resulted. It appeared that the higher the acidity, the higher the current density required for the deposition of chromium from its sulfate solution.

We next tried out the solution recommended by G. J. Sargent[16], 245 g./L. chromic acid plus 3 g./L. $Cr_2(SO_4)_3$. The anode was platinum and the cathode copper. The current density was 10 amp./sq. dm. (93 amp./sq. ft.) A bright crystalline deposit was obtained which proved satisfactory in all respects.

In the next experiment an iron cathode was used and two chromium anodes were used in place of platinum. The cell was allowed to run for 22.5 hr. The voltage at the beginning and end of the run was 2.3 v. The current density was 10 amp./sq. dm. (93 amp./sq. ft.). The deposit was grey, adherent, crystalline and satisfactory. The temperature of the electrolyte was 25° C.; there was no stirring aside from that brought about by the evolution of hydrogen. The chromium anodes showed no tendency to become passive, as would be ordinarily expected since

[16] *Loc. cit.*

chromic acid is such a strong oxidizing agent. This appears to be in direct contradiction to the statement made by Hittorf and quoted above. It is possible that the presence of the sulfate ions counteracted the tendency for the anodes to become passive. The anodes lost appreciably in weight and took on a smooth, silky appearance as compared with the original rough and scratched surface, which had been produced by grinding on an emery wheel.

We next made a series of runs varying the concentration of the chromic acid, but keeping the content of chromium sulfate and the current density constant. It was found that good deposits could be gotten on iron, using chromium anodes, anywhere within the range from 200 to 400 g./L. of chromic acid. The best concentration was found to be 245 g./L. chromic acid plus 3 g./L. chromium sulfate, which solution was designated as "C."

TABLE I.

Effect of Current Density on Deposit.

Solution: 245 g/L chromic acid, plus chromium sulfate 3 g/L. Room Temperature. Anodes, chromium. Cathode, Fe, with exposed surface of one sq. in. No mechanical stirring.

Sample	Time Min.	C. D. amp./sq. ft.	Voltage	Description of Deposit
1	120	90	2.3	Crystalline and adherent.
2	60	45	2.3	Surface barely covered.
2	120	125	2.5	Very good, bright, adherent.
4	120	144	2.5	Gray, crystalline.
5	60	345	2.9	Dull, adherent, tendency to form yellow coating.
6	120	540	3.5	Gray at first, then turned yellow and finally cracked.

Using this solution "C," the effect of current density was determined over the range from 2.7 to 54 amp./sq. dm. (25 to 500 amp./sq. ft.) Good deposits were obtained up to about 16 amp./sq. dm. (150 amp./sq. ft.) Above this the deposits were dark at first and after continued plating showed signs of cracking. The best current density to use for a bright adherent deposit proved to be between 10.8 and 13.4 amp./sq. dm. (100 and 125 amp./sq. ft.), with the electrolyte at room temperature. See Table I.

Cathode current efficiency tests were run with solution "C," using a copper coulometer in series, a current density of 13.8 amp./sq. dm. (125 amp./sq. ft.), chromium anodes and electrolyte at room temperature. A cathode current efficiency of 20 per cent was obtained for bright deposits. This, at first glance, would seem low, but is explained by the fact that together with chromium metal hydrogen is always evolved at the cathode.

Again using solution "C," a run was made to study the effect of temperature. The current density used for the room temperature run was 13.4 amp./sq. dm. (125 amp./sq. ft.) The deposit was satisfactory. On making a run at 55-60° C. and the same current density, no plate resulted after two hours operation, although the evolution of hydrogen at the cathode was quite rapid. However, upon doubling the current density a good plate resulted at this higher temperature.

The above phenomena suggest the following explanation: Hydrogen was evolved in all of our plating experiments where metallic chromium was deposited, and it seems that the formation of a protective layer of hydrogen gas over the chromium is essential. At higher temperatures the tendency for hydrogen to escape and leave the surface of the cathode is much increased. To counteract this loss, hydrogen must be evolved more rapidly. To do this a higher current density is necessary. On making a determination of cathodic current efficiency, using a copper coulometer, it was found that at higher current density, using a temperature of 55-60° C., there was no increase in efficiency. Hence, nothing is gained in employing the higher temperature.

Another determination was made with the solution temperature at 6° C. Again current efficiency measurements, as described above, showed no increase in efficiency was obtained by operating at this reduced temperature.

The theory above also explains why low current densities can not be used in chromium plating, for with low current densities the hydrogen evolved is not sufficient to produce the protective layer needed to furnish the reducing atmosphere for preventing the newly-deposited chromium from dissolving with the formation of a chromous salt.

PROPERTIES OF CHROMIUM PLATE.

Exposure for weeks to the corrosive atmosphere of the laboratory produced no effect on the chromium plate, whereas iron corroded rapidly. Chromium-plated iron immersed in tap water for a period of three weeks showed no signs of losing its luster or of a tendency to corrode. Dipping the chromium plate into hot sulfuric acid or hydrochloric acid caused it to dissolve. Boiling in hot concentrated nitric acid for 2 hours produced no appreciable effect on the chromium plate.

TABLE II.

Tests in Air Saturated with Vapors.

(a) Ammonia Vapor		*(b) Hydrochloric Acid Fumes*	
Sample	Loss in Grams/sq. cm./yr.	Sample	Loss in Grams/sq. cm./yr.
Cu	Gained in wt.	Cu	gained in wt.
Fe	zero	Fe	120
Cr on Fe	zero	Cr on Fe	1262
Al	zero	Al	377
Duriron	45	Duriron	70
(c) Conc. Nitric Acid Fumes		*(d) Hydrogen Sulfide Fumes*	
Sample	Loss in Grams/sq. cm./yr.	Sample	Loss in Grams/sq. cm./yr.
Al	19.4	Fe	23.6
Fe	2290	Duriron	gained in wt.
Duriron	10	Al	7.1
Cr on Fe	11.8	Cr on Fe	slight gain
Ni	475		

A series of corrosion tests on various metals in order to compare them with chromium plate under similar conditions was then undertaken. These consisted in exposing weighed samples in closed containers to air saturated with (a) ammonia, (b) hydrochloric acid, (c) nitric acid, and (d) hydrogen sulfide fumes for a period of 192 hours. At the end of this period the samples were again weighed and the loss or gain in weight per unit of surface per year was calculated. These are listed in Table II.

Table II shows that the chromium plate stands up well in ammonia vapor, nitric acid fumes and hydrogen sulfide fumes. It is practically on a par with duriron on exposure to nitric acid fumes. Hydrochloric acid vapor attacks chromium almost immediately.

TABLE III.

Electrolytic Corrosion Tests.

Current Density about 3.2 amp./sq. dm. (30 amp./sq. ft.)

Electrolyte	Anode Material	Loss in Grams/sq. cm./yr.
Conc. Nitric Acid.....	Cr Plated Iron.....	32.2
Conc. Nitric Acid.....	Iron	28.1
Conc. Nitric Acid.....	Aluminum	51.8
Conc. Nitric Acid.....	Duriron	0.623
Dil. Nitric Acid.....	Cr Plated Iron.....	108.
Dil. Nitric Acid.....	Aluminum	51.1
Dil. Nitric Acid.....	Duriron	0.102
Sea Water.....	Cr Plated Iron.....	113.
Sea Water.....	Iron	110.

Current Density 1.6 amp./sq. dm. (15 amp./sq. ft.)

Electrolyte	Anode Material	Loss in Grams/sq. cm./yr.
Conc. Nitric Acid.....	Cr Plated Iron.....	32.6
Conc. Nitric Acid.....	Iron	31.4
Conc. Nitric Acid.....	Aluminum	37.6
Conc. Nitric Acid.....	Duriron	0.453
Dilute Nitric Acid.....	Cr Plated Iron.....	31.8
Dilute Nitric Acid.....	Aluminum	37.5
Dilute Nitric Acid.....	Duriron	1.81
Sea Water	Cr Plated Iron.....	27.2
Sea Water.....	Iron	96.2

The effect of electrolytic corrosion of chromium plate as compared to other metals was then determined. The corrosive media used were solutions of concentrated nitric acid, dilute nitric acid (concentrated acid plus an equal volume of water) and sea water. Two runs were made, one using a current density of about 3.2 amp./sq. dm. (30 amp./sq. ft.) and the other using a current density of 1.6 amp./sq. dm. (15 amp./sq. ft.) Each extended

over a period of 24 hours, weighings of cathode and anode being made before and after each run. The results obtained are recorded in Table III.

Tables II and III show that chromium does not stand up under electrolytic corrosion nearly as well as it does under atmospheric corrosion. Of the materials tested, namely chromium-plated iron, ordinary iron, aluminum and duriron, the last showed smallest loss due to electrolytic corrosion.

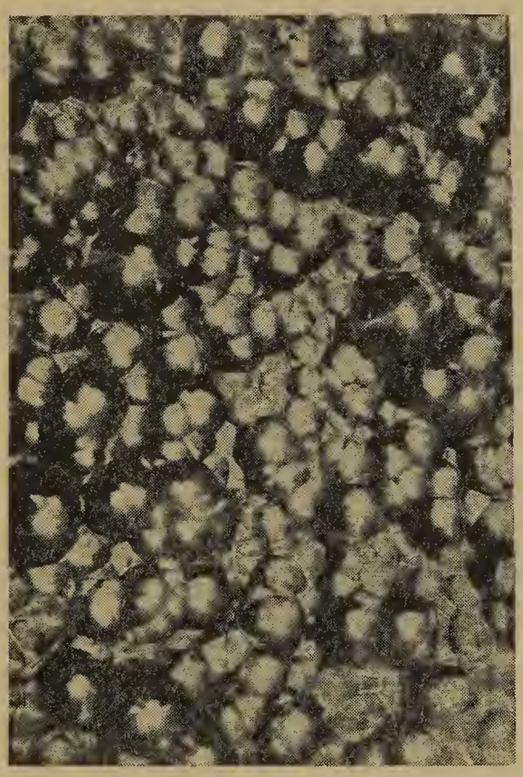


FIG. 1. x 300
Coarse crystals of bright deposit.

FIG. 2. x 300
Fine crystals of dull deposit.

We attribute the inability of chromium-plated steel to withstand electrolytic corrosion to a "breakdown" of the protective surface film by the action of the electric current. With the aid of the current the acid ions will pass readily through the surface film and attack the virgin metal beneath, whereas in the case of atmospheric corrosion the migration of the acid through the film is extremely slow in comparison.

Under the microscope the chromium plate is uniform and free from holes due to occluded gases. Photographs of a bright, coarse crystalline and a dull, fine crystalline plate are reproduced

in Figs. 1 and 2. The current density of the former was 13.4 amp./sq. dm., and of the latter 15.3 amp./sq dm.

Chromium plate has wearing qualities and hardness superior to ordinary iron, galvanized iron and tinned iron.

Chromium covered iron is not attacked by molten tin, zinc or brass, whereas ordinary iron disintegrates rapidly.

CONCLUSIONS.

1. Good, adherent deposits of chromium on iron were obtained, using solutions containing 3 g./L. chromium sulfate and from 200 to 400 g./L. chromic acid.

2. The cathode current density range for good deposits was found to be from 9.3 to 16 amp./sq. dm. (100-150 amp./sq. ft.)

3. Best results were obtained using Sargent's solution containing 3 g./L. chromium sulfate, 245 g./L. chromic acid, and a current density of 13.4 amp./sq. dm. (125 amp./sq. ft.) The anodes used were chromium. The solution was at room temperature and stirring in addition to that caused by the evolution of hydrogen was found unnecessary.

4. Chromium anodes in the above solution show no tendency to become passive even after long and continuous plating operations. Chromium anodes are cheaper than platinum and better than lead.

5. The simultaneous evolution of hydrogen with chromium deposition on iron is essential to good results. The hydrogen appears to protect the freshly discharged metal, and to counteract the great tendency of chromium to pass back to the chromous ion stage. This tendency is particularly marked in the strongly oxidizing medium of chromic acid.

6. Chromium plated iron and steel have a hard, bright, silver-like surface.

7. Chromium plated iron and steel resist atmospheric corrosion indefinitely.

8. Chromium plated iron and steel are resistant to the action of fumes of nitric acid, hydrogen sulfide and ammonia. They also resist the corrosive action of molten tin, zinc and brass.

9. Steel does not lose its temper during chromium plating.

10. Chromium plated iron does not resist electrolytic corrosion in mineral acids.

The writer wishes to express his sincere appreciation to Professor Colin G. Fink, under whose direction this investigation was carried out, and also to Professor Wm. Campbell and Dr. E. P. Polushkin for many valuable suggestions.

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DISCUSSION.*

H. K. Richardson[1]: The past year or so we have had considerable experience with chromium plating. It has been only a portion of our problem, that is, the chromium plating is a tool for us. The other part of our problem requires tests which sometimes take three months, so in between time we leave our chromium plating bath idle until such a time as we start over again. We are using a continuous process, chromium coating of nickel steel wires, drawing the wire at a low rate of speed, about 2 ft. per min., through this plating bath and taking the deposit from a solution which corresponds exactly to the solution given in the paper.

We did not stop to experiment with chromium plating. The bath given in the paper was the first tried; as it worked, we have done no further work on the study of chromium plating. However, we have experienced many trials with the continuous operation of this bath, and these difficulties are of interest; some are rather unusual but we will give them for what they are worth.

One is that as we increase the current density we get less and less deposit, until we get a brightly burnished, silver-like wire deposit. But we cannot determine accurately the thickness of plating on the wire; it is too small.

Confirming the observations of Mr. Schwartz, if we do not get an evolution of hydrogen, we do not get a deposit. Also, if we

* In the absence of the author the above paper was presented by Colin G. Fink.

[1] Westinghouse Lamp Co., Bloomfield, N. J.

do not have a dirty wire, we do not get a deposit. I do not mean a dirty wire going into the solution, I mean that if the wire coming out has not a dirty film on it, we have not much of a deposit on it. This film is probably the chromous-chromic sulfate noted by Sargent in his original paper.

The bath is temperamental in other ways. For instance, a newly made up bath unless made up from the purest of materials will not work the first time you use it. Yet, a bath which is made up of technically pure chromic acid, will start to work in a short time if the pure bath is allowed to stand around and a little dust settles in it. What the reason is, I cannot say.

The Sargent solution, as recommended by the author, does the best work. We find that a current density of about 75 amp. per sq. ft. (8 amp./sq. dm.) of the wire surface is satisfactory for our conditions.

The amount of sulfate in the bath we know is an important thing. Too high a sulfate content causes trouble, for the deposit commences to get thinner and thinner until it disappears. Another interesting thing is that you can not use sulfuric acid in place of the sulfate. Why, I have not found out.

Sometimes we find that we have to cool the solution, and other times we have to heat it in order to get decent deposits. The reason for that I am not prepared to say. If at the start the bath will not work cold, we just run a little steam through and it works all right. On the other hand if the bath is hot and will not work, we run a little cooling water through the steam coil to start it working.

Regarding the structure of chromium coated wire, when the underbody is thoroughly well prepared by anode cleaning, the coating adheres so strongly that we can draw the wire to a small diameter without cracking the surface, providing that the temperature is kept above a certain point. We have found that chromium coated wire does not oxidize up to 310° C. Above that we have not tried it.

Colin G. Fink[2]: I would like to confirm what Mr. Richardson has said. The coefficient of expansion of chromium as measured by Disch of the Reichsanstall is 94 as against 89 for ordinary glass.

[2] Head, Div. of Electrochemistry, Columbia Univ., New York City.

C. J. THATCHER[3]: I have had occasion to use large quantities of chromium solutions in the electrolytic regeneration of bichromate from chromium sulfate, and would like to call attention to the fact that, invariably, during the first oxidation by electrolysis of any new lot of a chromium compound there is a decided odor of chlorine, which is not noticeable in working with small quantities. This occurs with chromium compounds which are supposedly free from chlorine, and may have something to do with the "ageing effect" observed in chromium solutions.

S. C. LANGDON[4]: How pure was the chromium that you made by the Goldsmith process, and how thick were the deposits?

COLIN G. FINK: About 98 or 99 per cent Cr. Deposits up to an eighth of an inch were made. That is as far as we went. I do not see any reason why we could not increase this. We obtained a silver-like deposit, a fine, smooth deposit.

WM. BLUM[5]: The formation of a brownish cathode film, noted by Sargent and others, may be due to the fact that whenever hydrogen is discharged at a cathode, the pH of the adjacent solution increases. As the solution becomes less acid there is a tendency for the formation of basic compounds. A study of the hydrogen ion concentration of these solutions might throw light on the formation of the cathode film. If such films are colloidal, their formation will probably be greatly influenced by small amounts of impurities.

S. E. SHEPPARD and A. BALLARD[6]: (*Communicated*): An investigation of the electroplating of chromium, but chiefly on brass, has been proceeding for some time in this laboratory. We have thought it desirable to refer to our results, since they were obtained by following, with modifications, E. Liebreich's procedure[7], as so far published. Mr. Schwartz, in his valuable and interesting paper, does not appear to have compared Sargent's solution with Liebreich's, consequently we presume that the statement in his summary (3) "Best results were obtained using

[3] Chem. Engr. and Electrochemist, New York City.
[4] Asst. Prof., Northwestern Univ., Evanston, Ill.
[5] Chemist, Bureau of Standards, Washington, D. C.
[6] Res. Lab., Eastman Kodak Co., Rochester, N. Y.
[7] Z. f. Elektrochem., 27, 74 (1921).

Sargent's solution containing etc.," refer to modifications of Sargent's solution, and not to comparison of Sargent's with other solutions. Our solution was prepared by heating a chromic acid solution with moist chromium hydroxide. The results, using a rotating cathode, and a graphite anode enclosed in a canvas bag, were promising, and invited further work with chromium anodes, which is now in progress. Representative conditions and results were as follows:

Time in Min.	Current density		Voltage	Character of Deposit
	amp./sq. ft.	Amp./ sq. dm.		
120	93	10	5.3	Well adhering deposit of steel gray color
25	121	13	6.0	Very good adhesion; bright steel color
40	223	24	8.3	Poor adhesion; deposit flaked off easily

In general, the resistance of the chromium deposit to corrosion agreed with that described by Mr. Schwartz.

Colin G. Fink: I am at a loss to account for the high voltages obtained by Dr. Sheppard, when using graphite as anode. Their voltage is decidedly higher than the voltage we got using chromium anodes, voltages of about 2.5.

Wm. Blum (*Communicated*): Unpublished experiments made at this Bureau by J. R. Cain showed that when a piece of thin sheet plated with a chromium coating about 0.013 mm. (0.0005 in.) thick was cut so as to expose one edge, the latter was badly rusted in less than twelve hours immersion in distilled water. Zinc coated steel under similar conditions showed no corrosion on the edge for several days.

Colin G. Fink (*Communicated*): Referring to Dr. Blum's discussion above, it is important to note that zinc coated surfaces are readily marred by scratches or wear, but chromium plated surfaces are very hard and not readily scratched.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

THE USE OF MERCURY IN THE PURIFICATION OF ZINC SULFATE SOLUTIONS.[1]

By Samuel Field,[2] A. R. C. Sc. (London), and Wm. E. Harris.[2]

Abstract.

The need for zinc sulfate solutions of a high order of purity is first explained and the real advantages accruing thereto later indicated. The use of mercury as a purification agent is discussed in detail, this application being based on the well-known overvoltage of mercury against hydrogen. By amalgamating finely divided negative metals[3], such as zinc and aluminum, complete purification can be readily and economically effected even in strongly acid solutions. The mercury is added to the zinc liquors as mercuric sulfate, followed by zinc powder or zinc blue. The impurities are eliminated in preference to the hydrogen of the acid added. Economy of zinc is thus effected, and the method becomes applicable also for cases in which high acid content would prohibit purification owing to high consumption of zinc. An estimate of the costs of purification chemicals is included.

THE ELECTROLYTIC ZINC INDUSTRY.

The production of electrolytic zinc has now assumed such proportions that it is clearly evident that the initial experimental stages have been successfully passed; and that an industry has developed which will grow, and will certainly be a serious competitor with the distillation process. Though we do not feel it will immediately displace the older process, it will certainly assume greater prominence and will undoubtedly become the

[1] Manuscript received July 3, 1923.

[2] Northampton Polytechnic Institute, Clerkenwell, London, E. C. 1, England.

[3] The algebraic signs of potentials used throughout this paper are in accordance with those adopted by the Society. See Trans. Am. Electrochem. Soc., 36, 3 (1919).

standard process as the richer ores become less plentiful and the poorer ones have to be worked.

The large works which have been erected and are now working in America and Tasmania, indicate that the electrolytic process is a commercial success. In Great Britain, Norway, Belgium, Italy and northern Rhodesia the erection of electrolytic zinc plants is under discussion, even though steam may have to be used as the source of power.

The particular charm of the electrolytic process lies in the fact that practically any type of ore can be treated, even if the zinc content is as low as 21 to 25 per cent.

Sulfate, carbonate and other oxidized ores have all been successfully treated. It is interesting to note that the ores of the Rhodesian project are mainly silicates of zinc, where the whole of the silica is soluble, and from the solution high-grade spelter has been produced by the electrolytic process.

NEED FOR PURIFICATION.

It does not come within the scope of this paper to discuss all the stages in the production of electrolytic zinc. We wish rather to discuss in detail the purification of the crude liquor, and it will be sufficient to state that the ores, calcined or roasted, are leached with sulfuric acid and the silica is precipitated in the leaching vat. The resulting solution is then pumped through a filter press or otherwise clarified.

This crude solution may contain, in addition to zinc sulfate, the following impurities: Copper, cadmium, iron, nickel, cobalt, arsenic, antimony, manganese, aluminum, magnesium, vanadium, calcium, chlorides, nitrates and phosphates, according to the type of ore used.

It is now an established fact that successful and economical deposition of zinc from the sulfate solution can only be obtained from comparatively pure solutions, or, as they have been called, "commercially" pure solutions. Many attempts have been made to avoid this extreme purification by means of high current densities, revolving cathodes, cooling the solutions and the use of "dopes," but we are of the opinion that more money is spent in trying to evade the purity of solution than would be spent

in obtaining it. Absolute purity, that is, the elimination of all metals other than zinc, is not altogether desired, but the elimination of certain metals is desired, in fact is essential, and constitutes the most important step in the production of electrolytic zinc. The effects of a number of these metals are altogether out of proportion to the percentages usually occurring, and constitute the chief difficulty in the subsequent electrolysis. Any attempt to obtain a commercially successful zinc deposit from the crude or unpurified solution would be futile, but successful deposition from a purified solution is a matter of comparative ease. It is essential that such metals as copper, nickel, cobalt, antimony and arsenic be removed, as all these cause serious corrosion of the zinc during the subsequent electrolysis.

It has been stated that a variation of between 0.001 g./L. and 0.0003 g./L. of antimony made the difference between impossible and excellent cell room operations. Chlorides and nitrates should also be absent; both may be introduced into the solution by some of the reagents. While the former may also be in the ore, usually there is sufficient silver effectually to fix it during leaching.

On the other hand, such metals as cadmium and iron, while not causing serious corrosion, lower either the current efficiency of the process or the purity of the deposited zinc to such a degree that it is imperative that they be removed. Table I represents the relation between quantities of cadmium in the liquors and in the final zinc.

TABLE I.

Content of Cadmium.

Per Cent in Starting Solution	Per Cent in Cathode Zinc	Per Cent in Starting Solution	Per Cent in Cathode Zinc
0.003	0.06	0.02	0.36
0.006	0.12	0.10	1.62
0.01	0.17	0.20	3.61

In this experiment an 8 per cent zinc solution with 3 per cent of free acid was, by electrolysis, reduced to 3 per cent of zinc. The 5 per cent reduction of zinc would correspond to an increased percentage of the cadmium twenty times from the solution to

the metal. In any case only a trace of cadmium remained in the liquor after electrolysis.

Calcium, aluminum, magnesium and manganese have practically no harmful effects; in fact, in our opinion, the last two are distinctly advantageous to have in solution.

There is another aspect of this impurity question, which must not be overlooked. Such metals as copper and cadmium are removed by actual inclusion in the deposited metal, being deposited with it; but cobalt, nickel, iron, manganese, magnesium and the other metals mentioned are not deposited to any appreciable extent and accumulate in the solution. There are thus two distinct types of impurities which are harmful in their effects upon the cathode zinc recovery rate, those which deposit with the zinc and those which accumulate in solution. For successful work both types must be removed.

REQUIREMENTS FOR PURIFICATION.

It has already been stated that chlorides and nitrates can be introduced into the solution by impure or unsuitable reagents used in purification. For successful work, it is essential that whatever reagents are used in purification, they should be of such a character that they do not enter into solution, or if they do, they must have no detrimental effect upon the subsequent electrolysis or any other stage of the process. As an illustration of an unsuitable reagent, the authors know of a case in which sodium permanganate was used as a precipitant of cobalt, and it can hardly be surprising that the process came to a gradual stop due to the accumulation of sodium salts in the solution.

It should hardly be necessary to point out that reagents should be comparatively cheap, and of assured and easy supply. It is also desirable that the chemical reaction should be fairly speedy, and not require too great a call for manipulative skill on the part of the worker. This is particularly so where operations are conducted with hot solutions, as continued heating of a neutral zinc sulfate solution tends toward the precipitation of a basic zinc sulfate compound.

Published information as to the various methods of purification show that practically all conceivable chemicals possible, common

and uncommon, have been used and their use patented. The authors have covered a wide ground in their research for suitable purification methods, and consider those described in this paper to be the best and most economical for general use, and suitable for all types of ore.

GENERAL PRACTICE.

The universal method for precipitation of iron appears to be to oxidize it to the ferric condition by means of air or a manganese salt and precipitate with either lime or whiting. It has been our experience that if manganese is not present in the solution, in one form or another, the precipitation of iron is difficult, in fact almost impossible, when using air and whiting. Solutions made from impure zinc oxide, such as flue dusts and scrapings from zinc oxide workings, lead and iron blast furnaces, contain no manganese, and we found it practically impossible to eliminate the iron without the addition of manganese, in the form of crude liquor from the leaching of ores containing manganese. Copper and cadmium may be precipitated out of solution by zinc, either in tube mills or vats, using either zinc balls, scrap or powder.

Nickel. Of nickel there are few published data, apart from the details as described by one of the authors in the Transactions of the Faraday Society, **17** (1921). Nickel is one of the worst of the impurities causing corrosion, even worse than cobalt, and we found traces of it in practically every type of ore treated.

Arsenic and antimony. Although we have treated practically every type of ore from all parts of the world during our research work, we have never been troubled by these two impurities. We have found traces in the iron precipitate where evidently they had been precipitated with the iron. In any case they can not survive the process of eliminating cadmium and copper. We have been surprised at the amount of attention devoted to these two metals.

Cobalt. Cobalt has recently claimed considerable attention. Precipitation by means of lead peroxide or manganese dioxide, in the presence of a manganese salt, seems to be the usual method. However, nitroso-beta-naphthol has been mentioned as a precip-

itant, but we do not know of a case where it has been used on a commercial scale.

Vanadium. Vanadium is precipitated by means of zinc oxide as a zinc vanadate, after the vanadium has been reduced to the V_2O_3 stage by means of zinc powder.

Summary.

The general methods of purification can therefore be summarized as follows:

Iron, together with some arsenic and antimony, is precipitated by means of air and lime or whiting in the presence of a manganese salt.

Copper, cadmium, nickel, arsenic, antimony and vanadium by means of some form of zinc.

Cobalt by means of lead peroxide and a manganese salt.

DEFECTS.

It has already been stated that continued heating of zinc sulfate solutions with such reagents as lime, whiting, zinc powder or zinc oxide, especially in neutral or slightly alkaline solutions, tends to promote the precipitation of a basic zinc sulfate and entails a loss of zinc.

In our early work the plant procedure was as follows: A charge of crude solution, about 18 tons, was heated to about 70° C. in a deep tank. Air was then blown through, and whiting (calcium carbonate) added in the form of a thin creamy emulsion. The heating and agitation was continued at an average temperature of 90 to 95° C. for about 4 hr., when the whole of the iron was precipitated together with any silica, aluminum, arsenic and antimony which had escaped precipitation in the leacher. The solution was filtered, and the dry filter cake, on an average, assayed as follows:

	Per Cent		Per Cent
Zinc	25	SiO_2	2.2
Iron	3.2	Al_2O_3	0.06
CaO	12.8	Sulfur	13.8

Experiment showed that the zinc in this filter cake was very soluble in dilute sulfuric acid, while the iron was not. Use was

made of this fact in neutralizing the last traces of acidity in the leaching vat before precipitation of the silica to avoid gels.

The solution after the precipitation of the iron, was filtered and pumped into other vats and treated with zinc powder until the nickel was precipitated, it being found that the copper and cadmium were also entirely precipitated at the same time. The consumption of the zinc powder was high, in the neighborhood of 1 to 2 per cent in proportion to the solution. The operation was long, taking from 8 to 9 hr. for a 5 or 6 ton charge and there was frequently a heavy precipitate of the basic zinc compound.

Subsequent work showed that the addition of quite a small proportion of acid, previous to the addition of the zinc powder, completely eliminated the basic compound trouble and also cut the amount of zinc blue to as low as 0.2 per cent with a consumption of about 0.1 per cent acid, the time also being reduced to 5 or 6 hr. against 8 or 9 hr. for a 5 or 6-ton charge.

Though this method was a great improvement it still left much to be desired. We found, however, that if copper was absent from solution it was practically impossible to precipitate the cadmium and nickel, the zinc and copper appearing to set up electrochemical action and so aiding the precipitation of other metals.

Occasions arose where we actually added copper to the solution to bring about the precipitation of the cadmium and nickel, just as we had to add a manganese salt to bring about the precipitation of the iron in de-ironizing. This electrochemical action was so effective that we carried out a considerable amount of research work on it, and evolved a process in which mercury played a determining part.

SPECIFIC NEEDS.

The well recognized difficulties in the elimination of impurities from zinc sulfate liquors, thus call for improved methods which will be technically sound and commercially practicable. The increased rapidity of purification in the presence of acid is a matter of prediction amply borne out by experience. Increased acidity, however, involves increased consumption of zinc, in whichever finely divided form it may be used. The use of 0.1 per cent sulfuric acid followed by zinc powder entails a consumption of about 21 lb. of the powder per ton of cathode zinc for the

mere reduction of acidity. This is based on the assumption that, in electrolysis the 10 per cent zinc liquor is reduced to 3 per cent. In practice we have found 60 lb. of zinc powder a usual quantity. While the whole of this is not loss, it at any rate represents a depreciation of value from metal powder to zinc in solution.

Again, as has already been stated, the presence of copper was found to be advantageous in the removal of other and more negative impurities. If the production of electrochemical couples has any role in purification—and we believe it has—then a still less active metal might be even more serviceable. Arsenic has been suggested in one patent. Without speaking from experience we feel that this metal could be improved upon, as it carries at least one disadvantage which is shared by copper and other common impurities, *viz.*: that of promoting the evolution of hydrogen concurrent with the extravagant consumption of zinc.

Further, several salts are ruled out owing to their introducing impurities into the liquor which considerably accentuate the corrosion of the lead anodes. To steer clear of all the difficulties which could be enumerated is by no means an easy matter.

USE OF MERCURY.

When in 1918 we were face to face with this problem we felt that few reageants would adequately fill the bill. A brief consideration of the application of well-known couples in organic reductions, combined with a knowledge of the permanence of amalgamated zinc in sulfuric acid led one of the authors to the conclusion that a solution of the problem lay in the direction of the use of mercury. Indicative of this, a few simple chemical facts may be recalled.

1. The aluminum-mercury couple is a powerful reducer in organic work.
2. When impure zinc dissolves in sulfuric acid, there is evidence of ionization of the zinc at the expense of hydrogen, which is evolved at the numerous and minute traces of impurities.
3. Pure zinc is stable in pure dilute sulfuric acid, due apparently to the difficulty of evolving hydrogen against a zinc surface.
4. Amalgamated impure zinc possesses the stability of pure zinc.
5. The difficulty of evolving hydrogen against zinc is also experienced with mercury, and to even a greater extent.

Hence, a zinc-mercury couple or an aluminum-mercury couple held prospects of success. These were tried, with the most complete success. Turnings of the metal, not specially pure, were first tried, and were amalgamated or "quicked" by passing through a weak solution of a mercury salt. They were introduced into an impure sulfate solution, from which they eliminated the impurities in what appeared to us to be record time.

The efficacy of the zinc-mercury couple may be readily illustrated by a few simple experiments. Pure zinc dissolves only very slowly in pure dilute sulfuric acid. Fragments of electropositive metals, such as copper or platinum, induce solution partly according to the number of points of contact of the two metals. The addition of a trace of a soluble copper salt effects the precipitation of copper, and the numerous points of contact give rise to vigorous solution. While this is proceeding a solution of mercuric sulfate is added, and the mixture shaken. The metals become amalgamated and the action (gassing) at once ceases.

To this acid mixture quite large quantities of soluble copper compounds may be added, and with shaking or stirring the copper is completely precipitated without further evolution of hydrogen. The copper as an impurity is being eliminated with the theoretical weight of zinc, as any excess of zinc dissolving would give its equivalent of hydrogen evolved. The precipitation of all other impurities, save perhaps iron, may be similarly effected.

Again, aluminum turnings may be added to dilute sulfuric acid. The metal dissolves with rapidity. The addition of a mercury salt does not inhibit the solution of the metal. The action, however, is markedly reduced in violence, while positive metallic impurities are rapidly and completely eliminated. Indeed the action is still so virile, that decomposition of ordinary water containing sufficient impurities to give slight conductance continues. When amalgamated aluminum is used, zinc itself is precipitated from zinc sulfate solution, and this is in itself some guarantee of the prior purification of the solution. Similarly alloys of zinc and aluminum may be used. When aluminum is used in practice, its presence in the solution could not be deemed harmful—rather the reverse. Aluminum salts have been added by some workers in zinc deposition to improve the quality of the deposit. The alumi-

num would, however, be eliminated from the solution during the precipitation of the iron.

OVERVOLTAGE.

These principles justify a word here with regard to overvoltage, one phase of which is evidenced by the difficulties in evolving hydrogen against such metals as zinc and mercury, and other metals in a lesser degree. Quantitatively it may be defined as the "additional potential difference required for the deposition of the hydrogen against a cathode, over that required for a platinized platinum electrode in the same solution and at the same temperature." It has deservedly attracted a good deal of attention and is influenced by a number of conditions. Its importance in the electrolytic zinc industry may be realized, when it is stated that the successful electrolysis of acid zinc sulfate solutions could not possibly be accomplished, were it not for the beneficial influence of this phenomenon.

The fact that zinc ordinarily dissolves in sulfuric acid and displaces hydrogen, is, in itself, evidence of the readier decomposition of sulfuric acid in preference to zinc sulfate.

The thermochemical values of the compounds concerned are stated by Richards to be:

$ZnSO_4$ Aq.	248,000	cal. per gram molecule
H_2SO_4 Aq.	210,200	cal. per gram molecule
H_2O	68,360	cal. per gram molecule

Then the electrolysis of acid zinc sulfate solution with an insoluble anode takes the following chemical course:

$$\underset{248{,}000}{ZnSO_4\ Aq.} + \underset{68{,}360}{H_2O} = Zn + O + \underset{210{,}200}{H_2SO_4\ Aq.}$$

106,160 cal. per gram equation quantities.

$$\text{equivalent to: } \frac{106{,}160}{2 \times 96{,}540 \times 0.239} = 2.3 \text{ v.}$$

The corresponding value for water is 1.47 v. The decomposition of water proceeds against platinized platinum electrodes with a voltage only slightly above this value. The overvoltage is an

excess potential difference required to liberate the hydrogen at the same rate, using a cathode of another metal, say zinc. This value cannot be stated too precisely, except for equally precise conditions. It is a function of a number of conditions, two of which are current density and temperature.

The following figures are taken from the paper[4] by M. Knobel, P. Caplan and M. Eiseman which was presented before the last meeting of the Electrochemical Society.

Current Density Milliamp. per sq. cm.	Overvoltage Zinc	Current Density Milliamp. per sq. cm.	Overvoltage Mercury
2	0.716	0.769	0.8488
5	0.726	1.54	0.9295
10	0.746	3.87	1.006
50	0.926	7.69	1.0361
		38.7	1.0634

These values against zinc are sufficient to make it possible to deposit zinc in preference to hydrogen from an acid zinc sulfate solution upon a zinc cathode.

Again, overvoltage is increased with increased current density. This effect is a matter of long experience in practice. Hence in the end cells of a series in which the acid content is high and the zinc content correspondingly low, the current density can be easily and advantageously increased by decreasing the cathode area.

Temperature, too, influences overvoltage in the direction of reducing it. High temperature thus induces deposition of hydrogen with a lowered zinc efficiency. Hence attempts are frequently made to cool the solutions undergoing electrolysis. In spite of such a practice we are still of a conviction, born of experience, that such artificial cooling should be unnecessary. It should be possible to keep down the temperature of the solution, and still maintain good zinc cathode efficiency, without special cooling devices.

LABORATORY PURIFICATION.

These principles illustrate the application of overvoltage in zinc deposition. Their application in purification is based on the introduction of the zinc powder in an amalgamated form by passing it

[4] Trans. Am. Electrochem. Soc., 43, 55 (1923)

through a weak solution of mercury salt, or preferably by the addition of a mercury salt to the zinc solution followed by the zinc dust. Needless to add, mercuric sulfate is used, being easily prepared or procured, and introducing no new and injurious constituent into the zinc solution.

The zinc solution, which at this stage is nominally neutral, is acidified up to 0.1 per cent (one gram per 1000 cc.). This is effected with the acid liquors from the cells. This is followed by an addition of mercuric sulfate, equal to a mercury content reckoned on the zinc solution of 0.01 per cent. Zinc powder up to 0.15 per cent is now added and the whole stirred, preferably at an elevated temperature. The mercury is precipitated on the zinc, and with the exception of the iron all of the metallic impurities, including also cobalt, are eliminated. The overvoltage of hydrogen against mercury is thus applied in a new direction, and the impurities as they come out are amalgamated by the mercury. This hinders the solution of the zinc in the acid, reduces the consumption of zinc, and also facilitates precipitation of the impurities, and allows of even greater acidity being used without neutralization of the acid by zinc.[5] As a matter of fact, we have, on one occasion, found it necessary to remove impurities from zinc solution normally containing as much as 7 per cent of acid. This would be economically impossible with zinc powder alone. The mercury provided an easy and satisfactory operation.

From the slimes formed, which are readily separated, about one-half of the mercury can be readily recovered, and the metallic residue treated for the recovery of copper and cadmium when the amount of these metals justify it.

EXPERIMENTAL WORK.

Metallic zinc in any form is capable of precipitating copper, cadmium and nickel from zinc sulfate. In some experiments using zinc turnings we also precipitated cobalt from solution, but in this case we used a large excess of zinc. The most convenient form of zinc, offering maximum area for a minimum weight, is zinc powder, either in the form of atomized zinc or

[5] British Patent No. 162,030 (1919).

zinc blue (blue powder). Microscopic examination of the globules of zinc in the zinc blue showed that on an average they had a diameter of about 13 microns (0.0005 in.), from which we calculate that 454 grams (1 lb.) of zinc blue would have an effective area of 30.6 sq. m. (330 sq. ft.)

We also found that the precipitation of the impurities was considerably accelerated when the solution was heated. At 80° C. it took 5 to 6 hr. to precipitate the copper and cadmium, the nickel and cobalt being untouched. At 96° C. it took 3 hr. and the nickel was then considerably reduced but not completely precipitated, but the cobalt was untouched. At 100 to 103° C., all the four metals were entirely precipitated in 1 to 1.5 hr. All these figures were obtained on 5 to 6 ton charges.

In the amalgamation of the zinc powder, it was of course impossible to use metallic mercury, as the whole formed a paste. Hence, the addition of the mercury sulfate solution to the zinc solution just previous to adding the powder. By use of this amalgamated zinc powder a 6 ton charge of crude liquor, which had been previously de-ironized, was purified of copper, cadmium, nickel and cobalt with an expenditure of only 0.1 to 0.15 per cent of zinc powder.

PRESENT WORKS PRACTICE.

After leaching and precipitation of the silica, the solution while hot is pumped to the de-ironizing vat, where it is kept hot by means of steam and agitated with air, the iron being precipitated by means of whiting in the presence of a manganese salt. The solution is then filtered while hot and pumped direct to the de-nickelizing tank. If this operation is performed rapidly it will be found that the temperature is in the neighborhood of 80° C. Sufficient acid from the electrolytic cells is now added to give the solution an acidity of about 0.1 per cent. A previously calculated quantity of mercuric sulfate is now added to the solution, the proportions being about 0.01 per cent of mercury, just previous to adding the zinc powder. The zinc powder next added is from 0.1 to 0.15 per cent of the solution and, as the whole is agitated and heated to boiling, the impurities will be

seen floating, like a black scum, on the top of the solution. As soon as the solution tests nickel-free, it is carefully tested for cadmium, as we have found that the last traces of cadmium persist until all the nickel is down. When free from nickel, copper, cobalt and cadmium the solution is pumped through the filter press to storage tanks ready for electrolysis.

As has been already stated, it is possible to purify strongly acid solutions by the use of amalgamated zinc powder. A solution running 7 per cent H_2SO_4 was completely purified from copper, cadmium and nickel, using only 0.16 per cent zinc powder and 0.012 per cent mercury. Previous work on this solution, without the use of mercury, had been a failure, inasmuch as the acid consumed such a quantity of zinc as to make the process uneconomical. The solution after treatment with the amalgamated powder was electrolyzed, giving a high-grade zinc.

HIGHLY PURIFIED SOLUTIONS.

The advantages of highly purified solutions can not be overemphasized. They arise primarily from the increased current efficiency, and hence the reduction of the number of kilowatt hours required for deposition. This is accompanied by a reduction of "re-solution" or "corrosion" in the end cells, in which the acid content is at its maximum. The real aim of deposition will be the maximum reduction of the zinc content of the solution, within limits of expenditure of electrical power.

But a concomitant advantage must be considered. Illustrative of this, consider the case in which a 10 per cent solution (100 g. Zn per L.) is delivered to the electrolytic from the purification department. It may be acidified, by mixing with the end acid zinc solution to any desired extent, and electrolyzed. Of the outflowing liquors a volume is sent back to the "process" (or extraction) department, equal in volume to that of the 10 per cent zinc liquor received. The remainder circulates through the cell house only. Consider two cases:

A. In which impure liquors necessitate electrolysis proceeding no further than to yield a solution containing 4 per cent of zinc. Then the zinc extracted from the solution is $10 - 4 = 6$ per

cent, and 100/6 = 16.6 volume tons[6] of liquor will need to circulate through the whole of the process operations per short ton of zinc extracted. The volume is some measure of the capacity of the plant which will handle it. Moreover, if 4 per cent of zinc is left in the solution, then 100 tons of zinc solution will be purified—a not inexpensive operation—for every 6 tons of zinc cathodes produced.

B. Assume that in a more perfectly purified solution deposition may be successfully carried out down to 2 per cent of zinc. Then 10 — 2 = 8 per cent of zinc is extracted, and 100/8 = 12.5 volume tons of solution must circulate through the whole of the processes per ton of zinc extracted, again a measure of the diminished plant capacity to handle it. Further, the cost of purifying 100 tons of solution will now be shared by 8 tons of zinc extracted.

Such conditions lead us to the firm conviction that highly refined liquors constitute an ideal in zinc sulfate electrolysis.

COST OF PURIFICATION MATERIALS.

From the foregoing data and the present cost of the materials it will be easy for those interested to make an approximate estimate of the cost of materials for purification. Such estimates may easily provide occasion for criticism, but we nevertheless venture the following attempt under the conditions specified, dealing with chemicals only.

A short ton (907 kg.) of zinc cathodes is assumed to require 12.8 volume tons of zinc solution to be purified.

Consumption of zinc = 0.15 per cent.

Mercury used = 0.01 per cent, but one-half is recovered from slimes.

Mercury taken as 3 shillings per lb.

From the slimes much of the zinc which has not passed into the solution may be dissolved out, by treatment with sulfuric acid, subsequent to the volatilization of the mercury.

Zinc powder is reckoned at £50 per short ton and is assumed to depreciate to £25 per ton in the form of solution. Of the

6 A volume ton is volume of 2000 pounds of water.

zinc used, one-quarter is reckoned as dead loss and three-quarters to suffer a depreciation of £25 per ton.

Cost of Mercury.

$$\tfrac{1}{2} \times \frac{0.01}{100} \times \frac{14.3 \times 2240 \times 3}{1} = 4.8 \text{ shillings}$$

Cost of Zinc Powder.

$$(a)\ \tfrac{1}{4} \times \frac{0.15}{100} \times \frac{14.3 \times 50 \times 20}{1} = 5.36 \text{ shillings}$$

$$(b)\ \tfrac{3}{4} \times \frac{0.15}{100} \times \frac{14.3 \times 25 \times 20}{1} = 8.04 \text{ shillings}$$

Estimated cost of whiting	6.5	shillings
Purification cost per short ton of zinc cathodes	24.7	shillings

ACKNOWLEDGMENTS.

We gladly acknowledge that the foregoing work has been largely carried out at the Swansea, England, works of the British Metals Extraction Company, Limited, during the course of a long research both on a laboratory scale and a commercial unit on the electrolytic production of zinc. This unit had a zinc capacity of 1.5 tons per day and zinc was successfully produced from a wide variety of ores. Concurrently, laboratory work was kept in progress in the electrochemical laboratory of the Northampton Polytechnic Institute, Clerkenwell, London, E. C. 1.

DISCUSSION.*

C. A. Hansen[1] (*Communicated*); Mr. Field mentions, as others have mentioned, that low grade zinc ores, in Mr. Field's citation 21 to 25 per cent zinc, can be treated by the electrolytic process. This is no doubt true, but it is also true that low grade ores can be treated by the old retort process. As a matter of fact, it is uneconomical to treat a low grade ore directly by either process if it is at all reasonably possible to concentrate it first.

Under average conditions at present, the cost of handling a ton of finely ground high grade ore to and through the roasters is not

* In the absence of the authors the above paper was presented by Colin G. Fink.

[1] General Electric Co., Schenectady, N. Y.

less than $3.00. With lower grade ores the fuel consumption per roaster is generally higher, and the roaster output is generally reduced, so that $5.00 per ton is not an impossible corresponding cost for a 25 per cent zinc ore. This applies to McDougall, Wedge and Herreschoff types of furnace, and to electrolytic zinc plant practice; costs for Hegeler kilns or Ropp kilns and the like would be much higher.

The diluents in the low grade ores are finally weeded out of the electrolytic zinc plant *via* filters. The direct cost of carrying a ton of inert material through the zinc plant is high, and the indirect cost, through entrained solutions, is still higher, so that I doubt that $10.00 a ton is too high a value at which to set the penalty on inert diluents in an electrolytic zinc plant feed which contains no values in lead, silver or gold.

Taking matters as they are in the United States, I believe that concentration of zinc ores is rather more important from the wet plant standpoint than from that of the retort smelter. Mr. Field refers to the possibility of chlorine being present in zinc ores. I do not know of any zinc ores containing chlorine, but I understand that the Hobart electrolytic plant had difficulties arising through seepage of sea water into calcines shipped in bulk from Port Pirie. Chlorine attacks the lead anodes, causing them to slough; the resulting suspended lead (chloride-sulfate) is occluded in the zinc deposits; and the chlorine is set free in a vicious cycle.

Mr. Field refers to manganese salts as possibly being advantageous in the zinc cell. I have never been able to demonstrate to my own satisfaction that this is true. Electrolytic zinc made with lead anodes is never wholly free from lead, but the lead content of the zinc cathodes will increase more or less proportionately with additions of pure manganese sulfate to pure zinc sulfate solution. In general, the more manganese thrown out at the anode per unit of zinc deposited, the higher will be the lead to manganese ratio in the anode slime. I do not know how or why the manganese salts attack the anodes, but I assume that the lead finds its way into the cathode deposit as occluded suspensions of lead peroxide; the more peroxide sloughed by the anodes, the higher the percentage of lead in the cathodes.

Mr. Field refers to accumulation of sodium sulfate in solution

through use of sodium permanganate as reagent, as putting a limit to the cyclic use of solutions so treated. So far as I yet know, the use of permanganates for purification of zinc plant solutions, originated at Bully Hill. I still consider permanganate treatment of neutral solutions the most efficient prophylactic measure I know of for insuring a pure zinc sulfate solution, for setting up a standard of what can be done in the way of electrolyzing zinc sulfate solutions. However, I positively know that any such quantities of sodium permanganate as would put a limit to cyclic use of solutions through accumulation of sodium sulfate, would be quite out of question on the score of reagent costs; the reagent would cost rather more than the recovered zinc would sell for.

I do not believe that Mr. Field's opinion that nickel is worse than cobalt is generally shared, but this is not important any way since both are bad. So far as I yet know, I had the unenviable distinction of first getting into cobalt difficulties, at Bully Hill, in experimenting with Broken Hill concentrates. Cobalt is present in the Trail plant feed, and the only known outlet for it at Trail is the anode slime. By maintaining an excessive amount of manganese in the cell feed solutions, cobalt is kept within workable bounds, but improvement should be possible in the results obtained were the cobalt eliminated in the leaching plant. Cobalt is again cropping up in the Coeur d'Alenes. I know of no other instances on this continent where cobalt has given trouble. Nickel is more frequent in its occurrence, but I believe it has made itself less pointedly felt on the cost sheets.

I tried to precipitate cobalt and nickel with zinc, aluminum, and magnesium, with and without additions of copper salts, etc., without any material success. I did not then consider treatment of boiling solutions commercially practicable, and, as a matter of fact, I do not now consider such solutions practicable, unless the heat is furnished by the leaching reaction. Tainton has pointed the way to maintaining high leaching plant temperatures—by maintaining extraordinarily acid concentrations—and there is no question but that nickel and cobalt are precipitated by zinc in boiling zinc sulfate solutions. I do not know whether they can be quantitatively precipitated, and I know that boiling zinc sulfate solution will revert a whole lot of zinc dust to basic zinc hydrate.

The use of amalgamated zinc dust in this connection is extremely interesting.

In spite of Mr. Field's contrary experience, arsenic and antimony probably contribute more consistently towards keeping zinc plant executives interested in operating details than any other precious pair of impurities. There is one perfectly certain way of eliminating them in the leaching plant, but there are cost limitations which impair its beautiful simplicity somewhat. There is, I believe, no question but that both arsenic and antimony are adsorbed by freshly precipitated ferric hydrate, according to the Biltz partition law, the ratio of arsenic (or antimony) to iron in the precipitate varying with the concentration of arsenic (or antimony) in the solution in equilibrium with the precipitate. I experimented with this at Park City, in 1917, adding varying amounts of iron salt to zinc sulfate solutions containing antimony. The results were consistent with the data given in Table I. Arsenic is more readily adsorbed than antimony so I paid relatively little attention to arsenic. I have, however, added data for arsenic (not in zinc sulfate solutions) as taken from Biltz.[2]

TABLE I.

Adsorption of Antimony and Arsenic.

Precipitate and solution in equilibrium, 40° C.

Hansen		Biltz	
g. Sb per L.	Ratio Fe : Sb in ppt.	g. As per L.	Ratio Fe : As in ppt.
0.0100	3.9	0.0100	3.7
0.0050	5.7	0.0050	4.2
0.0020	8.5	0.0020	5.1
0.0010	13.0	0.0010	5.8
0.0005	21.4	0.0005	6.7
0.0001	43.2	0.0001	9.2

Badly roasted ore normally leached, or well roasted ore leached for excessive periods at high temperatures and relatively high acid concentrations, will yield much iron to solution. I think that this is why all the commercial zinc plants I know of had less trouble initially with arsenic and antimony than they experienced

[2] Berichte d. D. Chem. Ges., 37, 3138 (1904).

when the roasting department bugs had been set aside, and zinc extractions had crept up to the point where discussion of them was no longer avoided.

I am afraid that the above has been a discussion merely of the side remarks Mr. Field made in his paper. I know positively that the treatment of zinc plant solutions with zinc is expensive, and that it is inefficient. I believe that if all of the direct and indirect costs of zinc dust treatment were set down faithfully, the results would cause gnashing of teeth and generally upset the placid atmosphere of the zinc plant laboratories.

The use of mercury, as suggested by Mr. Field, seems expensive and the recovery of mercury will be more or less messy, but it has the extreme merit of being easily tested without heavy investment in equipment.

One of the first methods we used at Bully Hill for purifying solutions with zinc was a small tube mill filled with zinc shot. This tube mill was more efficient in its use of zinc, and removed cadmium more completely than any other equipment I have ever seen. I recommended the method to others, who tried it out on a similar scale and confirmed my good opinion of it. The result was that I built two mills, six feet in diameter and twenty feet long, and another built some twenty more or less similar mills. The large mills were not successful, since the heavy load of zinc compacted the charge and solution flowed over the charge instead of through it. These mills cost some $15,000 each—hence the pertinency of the above remark regarding investment in equipment. I still believe that the proper way to use zinc is to pass solution through a column of zinc shot; the shot must be stirred in some way to prevent precipitated metals from clogging the column, and the rub lies in obtaining a proper stirring mechanism.

Purification of Zinc Sulfate Solutions with Zinc.

1. Continuous solution flow through a zinc filled tube mill. Tube mill 12 in. inside diameter, 12 ft. inside length, 6 r.p.m. Mill filled with zinc which had been granulated by pouring molten metal into water. Flow rate through mill adjusted to a value well below that at which complete precipitation of copper and cadmium was effected. Each record in Table II covers from 25 to 125 tons of solution.

2. Continuous flow of solution through tube mill filled with granulated zinc. Tube mill 6 ft. inside diameter x 20 ft. inside length, 2.5 r.p.m. Approximately 25,000 lb. of zinc in the mill.

TABLE II.

Purification of Zinc Sulfate Solutions.

Series	1	2	3	4
Ore source of solution	Bully Hill	Mammoth Flue Dust	Judge	Broken Hill
Solution temp. ° C.	40	50	50	50
Flow rate, liters/hour:				
Maximum	680	800	285	560
Average	478	...	...	358
Impure feed solution:				
Cu, g./L.	3.02	2.77	1.78	0.128
Cd, g./L.	0.35	2.91	0.23	0.121
Zn, g./L. (approx.)	130	130	110	100
Acid	0.0	0.0	0.0	0.0
Precipitate recovered, washed, dried, but not acid treated:				
Cu, per cent	48.0	20.0	20.8	7.1
Cd, per cent	5.5	21.0	2.7	6.7
Zn, per cent	20.8	19.0	26.0	34.6
Granulated zinc consumed, weighed additions and mill balance:				
g./L. solution	4.67	7.12	4.60	1.08
Zinc accounted for in precipitate g./L.:				
Cu-Cd equivalent	3.34	4.38	1.97	0.21
Zn in precipitate	1.31	2.63	2.22	0.62
Zn not accounted for	0.02	0.11	0.41	0.25
Total	4.67	7.12	4.60	1.08
Zinc efficiency. Zinc consumed/Cu-Cd equivalent:				
Per cent	71.5	61.6	42.8	19.4

Solution treated 200,000 L. Judge Mining and Smelting Co., 1917. Data are given in Table III.

The small tube mill was perfectly reliable. The large mill was tricky; the zinc charge apparently compacted under its own

weight, and impure solution would come through. This unreliability of performance condemned it.

TABLE III.

Purification of Zinc Sulfate Solutions.

Average flow, Liters/hour	10,000
Impure feed solution:	
Cu, g./L.	0.050
Cd, g./L.	0.131
Zn, g./L.	69.5
Treated solution from filters:	
Cu, g./L.	0.0005
Cd, g./L.	0.0015
Precipitate recovered. Washed, dried, but not acid treated:	
Cu, per cent	4.48
Cd, per cent	11.55
Zn, per cent	40.50
Metallic zinc, per cent	0.00
Zinc accounted for in precipitate g./L. solution:	
Cu-Cd equivalent	0.127
Zn in precipitate	0.443
Total	0.570
Indicated zinc efficiency. Zn consumed/Cu-Cd equivalent:	
Per cent	22.3

3. Agitator tank with zinc dust additions. Devereux agitator, tank 12 ft. diameter x 14 ft. Batch system, about 15,000 L. of solution treated per batch. Tank filled, agitated, zinc dust added, agitation continued 40 to 60 min., solution settled 20 to 30 min. and decanted. About 500 lb. of zinc dust constantly present in the tank, sufficient being added with each charge to make up for current consumption. A record for the month of September, 1918, is given in Table IV.

4. Pachuca agitator with zinc dust additions. Practice much the same as with the Devereux agitator. Various zinc ores and concentrates from Guatemala were treated. The results are recorded in Table V.

5. Pachuca agitator. Instead of using zinc dust, a screen was laid at the base of the tank cone bottom. A bed of granulated zinc was laid on this screen and the air lift in the tank acted as a circulating pump. This was more rapid and more thorough in removal of cadmium than the zinc dust method, but the solu-

TABLE IV.

Purification of Zinc Sulfate Solutions.

	Analyses		
	Max.	Min.	Average
Impure feed solution:			
Cu, g./L.	0.440	0.060	0.208
Cd, g./L.	....	....	0.215
Zn, g./L.	....	....	....
Purified solution (cell feed):			
Cu	0.0005	0.0001	0.00018
Cd	0.0181	0.0045	0.0012
Zn	64.0	56.3	60.0
Precipitate recovered. Washed, dried, but not acid treated:			
Cu, per cent	6.43	3.55	5.028
Cd, per cent	6.80	4.00	5.150
Zn, per cent	50.2	43.3	45.92
Zinc accounted for in precipitate per liter of solution treated:			
Cu-Cd equivalent	....	....	0.340
Zn in precipitate	....	....	1.930
Total	....	....	2.270
Indicated zinc efficiency. Zinc consumed/Cu-Cd equivalent:			
Per cent	....	....	15.0

tion remained clear, the granulated zinc bed serving as a thorough filter as well as a thorough precipitant. The bed was bound to clog in continuous service so the method was abandoned.

The foregoing data are given not because they are particularly thorough, for they leave considerable to be desired in proving a complete story, but so far as I know little or no definite data on the subject have been published.

These data, together with a considerable amount of other evidence which is even less presentable, incline me to believe that percolation of solution through a column of zinc, in such manner that the containing tank remains filled with solution, is a more effective method of using zinc that the usual methods involving agitation with zinc dust.

TABLE V.

Purification of Zinc Sulfate Solutions.

Series	1	2	3	4
Calcines:				
Zn, per cent	38.0	35.5	57.1	40.8
Cu, per cent	10.9	1.91	1.78	0.74
Cd, per cent	0.17	0.18	0.29	....
Impure solution feed:				
Cu, g./L.	6.86	2.11	1.56	0.29
Cd, g./L.	0.12	0.20	0.35	....
Zn, g./L.	74.2	81.8	99.6	88.4
Recovered precipitate. Washed, dried, but not acid treated:				
Cu, per cent	33.0	26.0	19.7	13.15
Cd, per cent	0.6	2.4	4.4	....
Zn, per cent	37.3	42.4	41.8	47.0
Zinc accounted for in precipitate. Per liter of solution treated. Grams:				
Cu-Cd Equivalent	7.19	2.29	1.78	(0.30)
Zn in precipitate	7.76	3.58	3.26	(1.04)
Total	14.95	5.87	5.04	(1.34)
Indicated zinc efficiency. Zinc consumed/Cu-Cd equivalent:				
Per cent	48.0	39.0	35.3	22.4

The horizontal tube mill, as indicated above, is extremely efficient when it works, but the large mills required to make the method commercially applicable are tricky—I know of no better word to express the fault. The fault certainly lies in the zinc charge, and not in the mechanical design of the mill, nor in the expense of its operation and upkeep.

I should prefer a vertical tank with solution fed into the bottom and overflowing into peripheral launders, the upper portions of

the tank serving as a settling space. Some method of stirring the zinc to dislodge the precipitated metals is essential, and I doubt if a rotating stirring mechanism is practicable. I have often wondered whether vertical plungers operated through glands in the tank bottom could not be made to furnish sufficient agitation to serve the purpose. I believe that a little rubbing of the zinc granules against one another would be all that is necessary.

When zinc and zinc sulfate solution come together, whether in the tube mill or in the zinc dust agitator, hydrogen is liberated. Presumably, zinc hydroxide is formed, and the natural assumption would be that a molecule of zinc hydroxide would take to itself two molecules of zinc sulfate to form the basic sulfate. This, in turn, would lead one to believe that only one-third of the zinc found in the precipitate with which we are here concerned was derived from the zinc precipitant, and that the balance was derived from zinc sulfate. There is no evidence that this assumption is warranted at the temperatures used in collecting the given data—all in the range 40 to 60° C. I am inclined to believe, from unpresentable data, that the assumption is to some extent true for higher temperatures.

It is certainly true that the amount of zinc reverted to precipitate increases fairly rapidly with temperature. The amount of zinc reverted at a given temperature is more or less a function of time of contact and of contact area between zinc and zinc sulfate solution, and it is more or less independent of the amount of copper, cadmium, etc., precipitated, hence, "zinc efficiency" is a term which must be qualified by a fair exposition of all of the conditions involved in its determination.

SAMUEL FIELD and WILLIAM E. HARRIS (*Communicated*): C. A. Hansen's comments on this paper have been read with considerable interest by the authors, who would have been glad to answer more direct inquiries regarding the new scheme of purification proposed. While many of the comments offered do not directly touch the problem under discussion, they are, nevertheless, of interest as bearing upon a subject of present paramount importance in the zinc industry.

On page 483, Mr. Hansen seems to doubt that there is any

advantage due to the presence of manganese in the cell liquors. Yet on page 484 an excess of manganese in the feed is required to keep down the cobalt in the Trail solution. Indeed, it may be that for manganese added in an otherwise perfectly pure zinc sulfate solution, no great advantage could be claimed. In the industry, however, no such absolute purity is practicable. The term "pure solutions" then means commercially pure solutions, containing impurities within defined economic limits. Deleterious impurities, in minute quantities, may or even must be present, and Mr. Hansen has had some experience of this in the case of antimony. Wherever impurities, which are ordinarily removable by manganese per-compounds, are present, even in only minute quantities, the manganese present tends to be of advantage. We have frequently found it necessary to mix manganiferous solutions with others, which were free from this metal. Furthermore, some of our best zinc of 99.98 per cent purity was made from liquors which were quite muddy with precipitated manganese peroxide.

With reference to the disastrous effects of nickel and cobalt, one of the authors has elsewhere placed on record normal degrees of purification of solutions. By this purification nickel is reduced to 0.2 part per million, while cobalt need not be reduced to below 3 to 5 parts per million of solution. Incidentally, commercial purity has, of course, to be defined on some basis of costs of purification and that of current subsequently used in electrolysis. Furthermore, we see little possibility of antimony or arsenic passing the mercury system of purification.

We have made a careful study of purification by different methods. Nickel and cobalt are particularly difficult to remove in cold solutions. They are much more amenable to elimination with an increase of temperature. The quick handling of hot solutions does not necessitate great losses of heat.

A paper presented at the Forty-fourth General Meeting of the American Electrochemical Society, held in Dayton, Ohio, September 29, 1923, President Hinckley in the Chair.

ON THE SINGLE POTENTIAL OF ARSENIC AND ITS POWER TO REPLACE OTHER METALS IN SOLUTIONS.[1]

By Louis Kahlenberg[2] and John Vernon Steinle.[3]

Abstract.

1. The single potential of arsenic has been determined in a number of different electrolytes, and in general the results of previous investigators have been confirmed.

2. In making the single potential measurements arsenic electrodes were prepared in a number of different ways. It was found that a solid arsenic electrode, sawed from a large piece of arsenic, yields reliable results, and offers on the whole the best form of electrode for making the determinations. Electrodes prepared by electroplating arsenic on other metals were found to yield unreliable results in that they do not develop the true potential of pure arsenic.

3. Metallic arsenic was used to replace a number of metals, notably silver, copper, and mercury, from their compounds. The reaction which takes place in these cases may be written as follows:

$$6MX + 2As + 3H_2O = 6M + 6HX + As_2O_3$$

M represents a monovalent metal and X a monovalent acid radical. By slight modification so as to fit individual cases, this general equation represents what has been found to take place.

4. Arsenic was also replaced from its compounds by other metals. These replacement results could by no means in all cases have been predicted from a knowledge of the single potentials of the metals involved. While a parallelism between the replacement

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series of the metals and their single potential series is commonly acknowledged, a relation of cause and effect apparently does not obtain here. The power of a metal to replace another metal is a highly specific property which depends on the individual nature of the metals in question and also the liquids that are used in the experiments. Temperature and time are also important factors in conducting the tests.

INTRODUCTION.

The first work on the single potential of arsenic was done by Bernhard Neumann[4] in 1894. His results are a part of a larger research entitled, "Ueber das Potential des Wasserstoffs und einiger Metalle." He determined the difference in potential between metallic arsenic and an aqueous solution of arsenic trichloride, acidified with a sufficient amount of hydrochloric acid to prevent precipitation. The solution contained one gram-equivalent of arsenic trichloride per liter. The combination of arsenic in the arsenic trichloride solution was measured against the normal calomel electrode with the following result:

$$Hg \mid HgCl \text{ in } 0.5N\ KCl \mid \text{Equiv. } AsCl_3 \text{ in } HCl \mid As = 0.010 \text{ v.}$$

If the calomel electrode be taken as 0.56 v.[5] the single potential of arsenic in the equivalent solution of $AsCl_3$ would be 0.550 v.

In 1903 Jan v. Zawidski[6] confirmed this result. In a paper entitled "Zur Kenntnis der arsenigen Säure" he published measurements of the single potential of arsenic in an "aqueous" solution of arsenic tri-iodide (an excess of HI was probably present, though he does not state that such was the case). He found the single potential of arsenic in an equivalent normal arsenic tri-iodide solution to be 0.539 v.

In 1909 Le Blanc and Reichenstein[7] measured the potentials of

[4] Z. Physik. Chem. 14, 220 (1894).

[5] The value —0.56 v. for the normal calomel electrode is that determined by means of the drop electrode. The minus sign has been commonly attached to this value following the practice of Ostwald. The American Electrochemical Society has adopted the designation which makes the normal calomel electrode +0.56 v. as referred to the drop electrode and this has been adhered to throughout this paper. All of the single potentials have been expressed accordingly. See Trans. Am. Electrochem. Soc., 36, 3 (1919).

[6] Berichte, 36, 1435 (1903).

[7] Z. Elektrochem., 15, 261 (1909)

iodine, arsenic, antimony, and phosphorus in solutions of potassium hydroxide and in sulfuric acid.

N. A. Pushin[8] made a few measurements of the single potentials of arsenic alloys in the course of an investigation entitled "Potentials and Nature of Metallic Alloys". He used alloys of tin and arsenic and also of lead and arsenic.

While the present work was in progress in this laboratory, V. B. Marquis[9] in an article on the "Determination of the Electrolytic Potential and Overvoltage of Arsenic" published results of single potential measurements of arsenic in an alcoholic solution of arsenic trichloride. He employed an electrode formed by electroplating arsenic on copper. Results with such an electrode are, however, not reliable as will appear from the experimental work described below.

THE SINGLE POTENTIAL OF ARSENIC.

The arsenic electrodes used in the single potential measurements were prepared in four different ways, and C. P. arsenic was obtained from different sources so as to eliminate the possibility of results due to accidental impurities.

1. Arsenic electrodes were made by cutting suitable strips of the metal from a large lecture specimen by means of a hack saw. These strips were then carefully polished with emery cloth till a bright metallic luster was obtained. The connection was made by clamping a brass binding post to one end, and carefully coating this end with molten paraffin so that no liquid could come into contact with the brass. The connection is rather hard to make because arsenic is very brittle. This fact also makes it difficult to work with electrodes of this type without breaking them.

2. Arsenic electrodes were further prepared by pasting pure pulverized arsenic upon platinum foil, or some other suitable metal[10]. The attempt was also made to use Acheson graphite as a background, but this was not successful. The paste or binder employed was a solution of gelatine. Collodion was tried, but it

[8] J. Russ. Phys. Chem. Soc., 39, 528-656 and 13-54 (1908). cf. Chem. Abs., 2, 58-65 and 1415-1417 (1908).

[9] J. Am. Chem. Soc., 42, 1569 (1920).

[10] This method of preparing electrodes was suggested to C. A. Pierlé by Professor Kahlenberg. Pierlé, who worked in this laboratory, obtained good results in his investition of potentials of some oxides of uranium. cf. J. Phys. Chem., 23, 545 (1919).

always cracked off from the metallic surfaces. Only a fair degree of success was attained by using gelatine. The best results were secured by using a solution of cellulose acetate in pyridine. The process consisted of moistening platinum foil with the gelatine solution and then spreading pure, finely divided arsenic over the platinum and pressing the arsenic powder firmly upon the foil by means of a spatula. This electrode was then air-dried and finally dried in an oven a little below 100° C. The arsenic used was pure, re-sublimed material pulverized so as to pass through a 100-mesh sieve. Electrodes thus prepared by means of gelatine as a binder were short-lived, however, for the gelatine would soften and loosen from the platinum, and thus the potential of the latter metal rather than that of the arsenic would come into play. Different strengths of gelatine and drying at higher temperatures were tried, but no better results were obtained. At best these gelatine electrodes could be used for but one set of measurements. As already stated above, collodion was found to be entirely unsuitable as a binder.

A thick solution of cellulose acetate in pyridine yielded good results. The platinum foil was dipped into such a solution, then covered completely with the arsenic powder, which was firmly pressed to the foil by means of a spatula. After air drying, these electrodes were dried at 90° C. for an hour. They were then soaked in pure water for several hours to remove the pyridine, after which they were again dried for several hours. The entire process was then repeated so as to cover up any cracks that might have formed, and to replace edges that had split off. By means of this process electrodes were finally obtained which could be used successfully much longer than those prepared by using gelatine as a binder. Similar electrodes were prepared by using gold foil instead of platinum.

3. It was found that the finely powdered arsenic above mentioned could be pressed into sticks which are strong enough to serve as electrodes. A stick 2 cm. long and about 1 cm. in diameter was thus made by means of an ordinary pill press, such as is commonly employed in preparing samples for a bomb calorimeter. Copper wire was then carefully wound around one end of this stick of arsenic and coated with paraffin, so that no copper could

come into contact with the solution. The end of the stick which was dipped into the solution was, of course, free from paraffin. It was also found possible to make a flat arsenic electrode by pressing the pulverized arsenic between two copper plates in a strong vise. In this case, a brass binding post was clamped to the flat stick, the connection being coated with paraffin as before.

4. Finally, arsenic electrodes were prepared by depositing a heavy mirror of pure metallic arsenic on the inside of glass tubes by decomposing arsine as in the Marsh test. The apparatus was set up in exactly the same way as in making a Marsh test. Pure zinc,[11] hydrochloric acid and pure arsenic trichloride were used. The arsine was dried by passing it through a calcium chloride tube and then conducting it into a hard glass tube surrounded with a copper gauze. In this tube the arsine was decomposed by heating the tube to a good red heat. The arsenic thus liberated was passed into another hard glass tube upon whose inner walls it deposited forming a mirror consisting of a heavy layer of pure arsenic. Thus a thick coating of pure arsenic was formed on the inner walls of a hard glass tube 10 cm. long and 7 mm. in internal diameter. It is easy to make an electrical connection with this layer of arsenic, by introducing a strip of copper foil into one end of the tube and inserting a rubber stopper which presses the copper tightly against the arsenic. In using the electrode there is no danger of the solution coming into contact with the copper for the tube is sufficiently long. These electrodes gave good results. However, their life is short, for when in contact with a solution the arsenical layer slowly peels off from the walls of the glass tube.

The potentials were measured by means of the Poggendorff compensation method, a sensitive galvanometer serving as zero instrument. Cadmium standard cells were used in making the comparisons. These cells had an e. m. f. of 1.01883 v. and 1.01885 v. respectively at 17° C. For the purpose in hand it was quite sufficient to measure the potentials in question to a millivolt, though the apparatus was capable of yielding a higher degree of accuracy. The half-normal calomel electrode was prepared in the customary way[12] and its potential was measured against several

[11] The zinc used was of the highest purity. It was of Schuchardt's manufacture. This zinc was used in all of the experiments described in this paper.

[12] Ostwald-Luther, "Physico-chemische Messungen", pp. 441-444.

combinations, *viz*: zinc in normal zinc sulfate solution, copper in normal copper sulfate solution, and zinc in normal zinc chloride solution. The results checked well with those of B. Neumann[13] and those compiled by R. Lorenz[14], so that the calomel half-cell was perfectly reliable. Its value was taken as 0.577 v. as referred to the drop electrode.

In order to check the results of Neumann and of Zawidski above mentioned, the single potential of arsenic was first measured against solutions of $AsCl_3$ and AsI_3, containing in each case one gram equivalent per liter of the salt. Just enough of the free hydrohalogen acid was added in each case to prevent precipitation. The results obtained are given in volts in Table I. Eight different electrodes were used as indicated in the table.

TABLE I.

Single Potentials of Arsenic Using Different Electrodes.

No.	Description of the Electrode	Single Potentials of Arsenic in Solutions of 1 gram equivalent per L.	
		$AsCl_3$	AsI_3
1	Electrode, sawed from large piece.....	0.554	0.540
2	Duplicate of No. 1.....	0.553	0.542
3	Pressed pill of arsenic coated with paraffin	0.549	0.538
4	Arsenic plated on inside of glass tube. (Marsh method.).....	0.552	0.544
5	Pressed stick of arsenic.....	0.548	0.537
6	Powdered arsenic pasted to platinum with gelatine.....	0.544	0.533
7	Same as No. 6 using pyridine solution of cellulose acetate for binder.....	0.551	0.541
8	Same as No. 7, using gold in place of platinum	0.551	0.543

The results in Table I show that the figures obtained by Neumann and by Zawidski are quite reliable for the respective solutions with which they worked. Moreover, the figures obtained

[13] *loc. cit.*
[14] Lorenz, "Electrochemisches Praktikum," p. 177.

with the eight different electrodes check about as well as could be expected in work of this kind. Electrode No. 6 in which gelatine was used as a binder was rather low; but, as already stated, the gelatine loosens up in the aqueous solutions, and so a lower reading would naturally be obtained. Electrode No. 4 by the Marsh test method probably represented arsenic of the very highest purity, but the deposit peels off from the glass soon after it has been introduced into the solutions. The most practical of all of the electrodes used is No. 1, namely, that sawed from a large piece of arsenic, and the results in Table I demonstrate that it yields a reliable potential. In the work of measuring the single potential of arsenic in various solutions, this type of electrode was consequently finally used. However, it was thought best to check the different electrodes mentioned in Table I once more in another electrolyte, to see how they compared with one another. The electrolyte chosen for this purpose was a normal NaCl solution which was saturated with As_2O_3. The results of the single potentials found are given in Table II. The electrodes are numbered as in Table I.

TABLE II.

Single Potential of Arsenic in a Normal Solution of NaCl Saturated with As_2O_3.

Electrode No.	Single Potential in volts.
1	0.365
2	0.365
3	0.362
4	0.361
5*	
6	0.360
7	0.364
8	0.363

* Could not be used.

The results agree about as well as one could expect. It should be observed that when an arsenic electrode is introduced into a normal NaCl solution saturated with As_2O_3 it requires from 7 to 10 min. for the potential readings to become constant. In all other solutions that were used in this work, the readings became constant in 1 or 2 min.

In the case of the platinum and gold electrodes that were coated with arsenic, it might be questioned if the potential of the former metals does not also manifest itself in making the measurements. To set this question at rest, the single potentials of pure gold and platinum were measured in normal sodium chloride solution saturated with As_2O_3 and the results found were 1.004 v. and 0.943 v. respectively. These noble metals are positive toward the calomel cell, whereas when they are coated with arsenic the polarity reverses and the single potentials 0.364 v. and 0.362 v. are obtained. To settle the matter still more conclusively, arsenic powder was pasted on an arsenic electrode that was sawed from a large piece of arsenic. The electrode so prepared yielded the single potential of 0.362 v.

TABLE III.

Comparison of Single Potentials of Electrodes of Solid Arsenic and of Arsenic Plated on Copper.

Description of the solution	Type of electrode	
	Solid As volts	As plated on Cu volts
½ equiv. K_3AsO_4 per L.	0.381	0.333
½ equiv. Na_3AsO_4 per L.	0.381	0.326
½ equiv. Na_3AsO_3 per L.	0.054	0.283
1 equiv. KCl saturated with AS_2O_3	0.365	0.331

After the above work had been completed, the article of Marquis[15] appeared. He used electrodes prepared by electroplating copper foil with metallic arsenic from a solution containing 5 g. of As_2O_3 in 300 cc. of 33 per cent hydrochloric acid solution. A current density of 0.15 amp./sq. dm. was used. The length of time of plating was not stated. The single potential of the electrode so prepared was measured against arsenic trioxide dissolved in alcohol. Since the single potentials of arsenic and copper lie quite close to each other, it seemed advisable to investigate the reliability of an arsenic electrode prepared by electroplating that metal on copper. In preparing such an electrode, the method described by Marquis was followed, and a good coating was ob-

[15] *loc. cit.*

tained. Table III gives the results of the single potentials of a solid arsenic electrode, as compared with one of arsenic electroplated on copper.

The results with the different electrodes clearly do not agree well, showing that the electrode of arsenic plated on copper does not give the true single potential of arsenic.

To follow this matter somewhat further, arsenic was electroplated on a number of different metals and the potentials which such electrodes developed were measured and compared with the potentials developed by the unplated metals. The results are given in Tables IV and V.

TABLE IV.

Single Potentials Expressed in Volts.

Metals	Half equivalent solutions in water			
	Na_3AsO_4		K_3AsO_4	
	Unplated	Plated with As	Unplated	Plated with As
Gold	1.026	0.452	1.031	0.450
Platinum	0.983	0.446	0.980	0.446
Palladium	0.861	0.416	0.870	0.418
Silver	0.643	0.365	0.644	0.373
Copper	0.370	0.326	0.371	0.333
Tin	0.111	0.228	0.112	0.230
Lead	—0.083	0.241	—0.080	0.249
Nickel	0.216	0.234	0.241	0.238
Cobalt	0.127	0.209	0.131	0.210

TABLE V.

Single Potentials Expressed in Volts.

Metals	½ Equiv. Na_3AsO_3 in H_2O		As_2O_3 saturated in 1 equiv. KCl	
	Unplated	Plated with As	Unplated	Plated with As
Gold	1.031	0.198	1.004	0.391
Platinum	1.010	0.221	0.943	0.406
Palladium	0.892	0.229	0.872	0.380
Silver	0.683	0.210	0.694	0.398
Copper	0.294	0.283	0.375	0.331
Tin	0.094	0.180	0.116	0.182
Lead	—0.051	0.121	—0.028	0.209
Nickel	0.218	0.180	0.228	0.416
Cobalt	0.119	0.208	0.126	0.398

When Tables IV and V are compared with Table III, it is evident that when arsenic is electroplated on different metals, the resulting electrodes do not develop the true potential of arsenic. In fact the potentials of such electrodes are not at all the same toward the same solution. All that can be said is that the nature of the underlying metal upon which the arsenic is electroplated apparently exerts itself and influences the potential actually observed. It should perhaps be added here that in all cases in Tables IV and V beautiful, blue black deposits of arsenic were obtained and, indeed, microscopic examination of each arsenic plated electrode revealed no flaws in the coating.

TABLE VI.

Single Potentials of Solid Arsenic Electrode in Different Solutions.

Description of the Solution	Single Potential Volts
Equivalent $AsBr_3$ per L. (+HBr)	0.544
Saturated solution of As_2O_3 in Equivalent Na_2SO_4 per L.	0.349
½ Equivalent K_3AsO_4 per L.	0.381
½ Equivalent Na_3AsO_4 per L.	0.381
½ Equivalent Na_3AsO_3 per L.	0.054
Copper Arsenate saturated in ½ Equivalent KCl per L.	0.367
Copper Arsenite saturated in ½ Equivalent KCl per L.	0.365
Paris Green saturated in ½ Equivalent KCl per L.	0.351
½ Equivalent solution of As_2S_5 in $(NH_4)_2 S_x$ per L.	0.052
Ammonium Polysulfide, Equivalent $(NH_4)_2S_x$ per L.	—0.065

TABLE VII.

Single Potentials of Solid Arsenic Electrode in Different Solutions.

Solutions in ½ *N* HCl	Single Potentials	
	As	Cu
Copper arsenate, saturated	0.367	0.332
Copper arsenite, saturated	0.365	0.358
Paris green, saturated	0.351	0.345

Having thus definitely determined that the most reliable results are obtained when a solid arsenic electrode such as electrode No. 1, Table I, is used, the single potentials of such an electrode in a

number of other solutions of arsenical compounds which are of practical moment were measured. The results obtained are shown in Tables VI, VII, and VIII.

TABLE VIII.

Single Potentials of Solid Arsenic Electrode in Different Solutions.

Solutions of the Sodium Salts of:	Single Potential in Volts — Fraction of Molecular Weight per L.		
	½	¼	⅛
Arsanilic Acid NH_2 ⟨⬡⟩ $AsO(OH)_2$ *i. e.*, Atoxyl NH_2 ⟨⬡⟩ $AsO(OH)ONa$	0.152	0.160	0.167
Para-hydroxy-arsenic Acid HO ⟨⬡⟩ $AsO(OH)_2$ (Na Salt)	0.090	0.095	0.100
Glycine Arsanilic Acid $HOOCCH_2NH$ ⟨⬡⟩ $AsO(OH)_2$ (Na Salt)	0.141	0.146	0.152
Secondary Arsanilic Acid NH_2 ⟨⬡⟩ As(=O)(OH) ⟨⬡⟩ NH_2 (Na Salt)	0.211	0.223	0.234
Aceto-arsanilic Acid CH_3CO . NH ⟨⬡⟩ $AsO(OH)_2$ *i. e.*, Arsacetine CH_3CO . NH ⟨⬡⟩ $AsO(OH)ONa$	0.129	0.141	0.152

An inspection of Table VI shows that the single potential of arsenic in $AsBr_3$ lies between that developed in $AsCl_3$ and AsI_3 (Table I), which was to have been expected. The solution of

As_2O_3 in Na_2SO_4 yields much the same potential as that of As_2O_3 in NaCl. Compare Table II. The potential of arsenic in sodium arsenate solutions differs from that in corresponding sodium arsenite solutions by about 0.30 v. which was to have been expected, since the solutions in which arsenic has a valence of three are reducing agents. The sodium arsenates yield the same potential as the potassium arsenates of equivalent strength, as one would expect. The solutions of the arsenates and arsenites of copper yield only slightly different results, because these salts are only sparingly soluble. Compare Tables VI and VII. Indeed, the potentials of these sparingly soluble salts are not very different from those of a salt solution saturated with the sparingly soluble As_2O_3, (Table II).

In Table VII are given the single potentials of arsenic in three cases, as compared with those of pure copper. Copper being lower in the electrochemical series than arsenic, the results are such as one would look for. However, it is clear that copper and arsenic lie very close to each other in the electrochemical series. Compare results in Table VII.

In ammonium sulfarsenate solution (Table VI) the potential of arsenic is quite different from that in the other cases, probably because such a solution is powerfully alkaline. Indeed, the potential toward an ammonium polysulfide solution is actually different in sign, as Table VI shows. It was found by actual measurements, which were repeatedly checked, that the solid arsenic electrode developed a single potential of 0.129 v. in a half normal NaOH solution, and a potential of 0.583 v. in a half normal HCl solution, while in a half normal NaCl solution the voltage was 0.547. This shows that the acidity or alkalinity of the solution has an effect on the potential, and that alkalinity produces a far greater change than acidity.

Finally, in Table VIII are given the measurements of single potentials of the solid arsenic electrode in solutions of five organic compounds of arsenic, which have found application in therapeutics. Three different concentrations of each solution were used as indicated in the Table. In each case the potential increases regularly with the dilution as one would expect. Some relations between constitution and potential are apparent, for the substitu-

tion of OH for NH_2 results in an arithmetically lower single potential. It was thought that possibly a relation between the single potentials found and the known toxicity of these compounds might be detected, but such is not the case. According to the Nernst theory of e. m. f. arsenic would be less negative toward a solution the more "arsenic ions" the solution contains. If it be assumed that the toxicity of an arsenic solution depends upon the concentration of the "arsenic ions," one would conclude from Table VIII that arsacetine and the sodium salt of glycine arsanilic acid are about equally toxic, and that atoxyl is less toxic than either of these. The facts are, however, that glycine arsanilic acid is much less toxic than atoxyl or arsacetine.

THE POWER OF ARSENIC TO REPLACE OTHER METALS.

The electric potential of a metal has commonly been considered as directly connected with the power of the metals to replace other metals in compounds and solutions. Extensive investigations on the electrochemical series of the metals and their power to replace one another have been carried out in this laboratory,[16] but arsenic has hitherto not been subjected to special study.

Arsenic lying on the border line between the metals and the non-metals, might well be expected to appear below the other metals in the electrochemical series, but such is not the case. According to LeBlanc[17] the electrochemical series is:—lead, tin, hydrogen, antimony, bismuth, *arsenic,* copper, silver, mercury, while according to Ostwald[18] the order is lead, hydrogen, antimony, bismuth, *arsenic,* copper, mercury silver, palladium. The latter order is probably the more correct one; but in any case, it is clear that there is disagreement as to the relative position of arsenic in the electrochemical series. The fact is that the nature of the electrolyte used is also an important factor in determining the relative position of the metals in the electrochemical series, especially of those metals that lie about in the middle of the series.

In the experimental work of displacing other metals by arsenic, the purest C. P. metals and chemicals were employed throughout;

[16] Kahlenberg, Trans. Am. Electrochem. Soc. **18**, 103 (1910); *ibid.* **6**, 53 (1904); Kahlenberg, J. Phys. Chem. **6**, 6 (1902); Kahlenberg and Schlundt, *ibid.* **6**, 447 (1902); Kahlenberg, Z. Phys. Chem. **46**, 63 (1903); Mathews, J. Phys. Chem. **9**, 641 (1905); Sammis, *ibid.* **10**, 593, (1906); Gates, J. Phys. Chem. **15**, 97 (1911).

[17] Textbook of Eletrochemistry 7th German edition.

[18] Outlines of General Chemistry 3rd Eng. Trans. p. 462.

they were usually of Kahlbaum's or Merck's manufacture. The replacements were carried out in clean, glass stoppered bottles of about 50 cc. capacity. A piece of bright, clean metallic arsenic weighing about 3 g. was placed in each bottle and then a 10 per cent solution of the salt in question was added,[19] When the salt was not soluble enough to enable one to make a 10 per cent solution, a saturated solution was used.

Immediately on introducing the arsenic into the liquid an observation was made to see if action was instantaneous. Further observations were then made from time to time, some of the experiments being continued for several months. Each time the solutions were tested to see if arsenic had replaced the metal in the solution. If aresnic was found, tests were made to ascertain if the replacement was complete, and efforts were made to replace the metal completely by adding more metallic arsenic. Upon completion of the replacement, the solution was evaporated to dryness and the residue examined with a microscope. Arsenic trioxide forms beautiful regular octahedra which are easily recognized. If in the course of the microscopic examination of the residue anything other than these characteristic crystals was observed, a further examination was made. The details of the results of the replacement experiments follow.

Silver.

Silver nitrate, ($AgNO_3$)—100 g. per L. solution in water. An immediate deposition of silver in the form of a dull, white, smooth plating with an accompanying evolution of brown fumes of nitrogen dioxide (NO_2) was noted. The evolution of nitrogen dioxide was more marked when finely divided arsenic was substituted for the larger piece. In the latter case, the reaction mixture warmed up slightly and became light green in color. Even after standing for several months in contact with the metallic arsenic, the solution still contained a large amount of silver. Upon evaporation to dryness, small crystals of arsenic trioxide were found

[19] In the data given below the concentrations approximately expressed in grams per liter in accordance with the usage of the American Electrochemical Society. In the final interpretation of the replacement results, it makes no difference whether the solutions were saturated or of some other strength, for replacements either take place or not regardless of the concentration of the solution.

among the larger crystals of silver nitrate. The reaction may be expressed by the following equation:

$$3AgNO_3 + 4As = 2\ As_2O_3 + 3Ag + 3NO.$$

Silver sulfate, (Ag_2SO_4)—saturated solution in water. Light gray, metallic silver of a flocculent nature was immediately deposited, and all of the silver was displaced from the solution within a few hours. Microscopic examination after evaporation to dryness showed nothing but the characteristic arsenic trioxide octahedra. The reaction is:

$$3Ag_2SO_4 + 2As + 3H_2O = 6Ag + 3H_2SO_4 + As_2O_3$$

Silver nitrite ($AgNO_2$) —saturated solution in water. The silver was entirely thrown out of solution within a few hours in the form of a light gray, fluffy deposit. The replacement was accompanied by the evolution of oxides of nitrogen. The residue upon evaporation consisted entirely of arsenic trioxide. This equation expresses the reaction:

$$6AgNO_2 + 2As = As_2O_3 + 6Ag + 3NO_2 + 3NO$$

Silver acetate (CH_3COOAg)—saturated solution in water. A heavy yellow precipitate was formed instantaneously upon the addition of metallic arsenic. Within twelve hours, this precipitate had entirely disappeared, and the arsenic was coated with a white, fluffy deposit of silver. This white precipitate turned gray and curdy after standing for a week, at the end of which time, the silver had been entirely replaced from the solution. The arsenic was in solution in the form of arsenious acid. The equation for the reaction follows:

$$6CH_3COOAg + 2As + 3H_2O = 6CH_3COOH + 6Ag + As_2O_3$$

Silver tartrate ($C_4H_4O_6Ag_2$)—saturated solution in water. No immediate action was observed. After standing three days, all of the silver had been replaced by arsenic, and was precipitated as a tough, gray curdy deposit. The arsenic was found in the solution as arsenic trioxide. The reaction may be expressed as follows:

$$3C_4H_4O_6Ag_2 + 2As + 3H_2O = 3C_4H_4O_6H_2 + 6Ag + As_2O_3$$

Silver cyanide ($AgCN_6$)—100 g. per L. solution in potassium cyanide solution, $KAg(CN)_2$. Only after standing for one month, was a sufficient amount of silver deposited to form a thin coating of white metallic silver, which adhered tightly to the arsenic. Although the solution still contained quantities of silver, no more could be displaced, even when more arsenic was added and the mixture allowed to stand 6 months. No trace of arsenic trioxide could be found on evaporation. In this case, the arsenic had probably directly replaced the silver, to some extent, to form a double cyanide corresponding to potassium ferricyanide ($K_3Fe(CN)_6$). The reaction probably takes place as indicated by this equation:

$$3K\,Ag(CN)_2 + As = K_3\,As\,(CN)_6 + 3Ag$$

Silver fluoride (AgF)—100 g. per L. solution in water. A dirty yellow deposit was immediately formed on the arsenic, but it dropped off in the form of a granular precipitate of silver. Currents were observed to rise from the arsenic, and a glass stirring rod placed in their path was etched. No gas was evolved. Upon evaporation, hydrofluoric acid gas was detected, and the arsenic was left in the form of octahedral arsenic trioxide crystals. The replacement and hydrolysis may be expressed by this equation.

$$6AgF + 2As + 3H_2O = 6HF + 6Ag + As_2O_3$$

Silver nitrate ($AgNO_3$)—100 g. per L. solution in pryridine. The arsenic was slowly coated with a uniform, adhering deposit of white metallic silver, and not in form of trees, as is usually the case with silver nitrate solutions. The silver was completely replaced from the solution within a week. The arsenic was held in solution as arsenious acid. The equation expressing this reaction is the same as that of the solution of silver nitrate in water. Hydrolysis does not enter into this reaction; therefore, arsenic trioxide can be formed in solution without the presence of water.

$$3AgNO_3 + 4As = 2As_2O_3 + 3NO + 3Ag$$

Silver chloride (AgCl)—saturated solution in pyridine. All of the silver was deposited within a day as a shiny coating of silver

adhering to the arsenic. Upon evaporation, only arsenic trichloride remained, there being no water present to hydrolyze it. The reaction may be expressed as a simple replacement.

$$3AgCl + As = AsCl_3 + 3Ag$$

Silver sulfate (Ag_2SO_4)—saturated solution in pyridine. The solution turned black, and a black precipitate was formed on the bottom of the container. A silver mirror was formed on the side of the container facing the sunlight. The solution still contained silver after standing 6 months, but no arsenic could be detected. The action seemed to be entirely due to the light.

In soultions of *silver palmitate* and *stearate* in acetone and in anhydrous ether, arsenic would not replace silver at all.

From the experiments on silver salts it is evident that silver is readily replaced from aqueous solutions of most of its salts by arsenic. In many cases, silver is completely replaced, while arsenic goes into solution as arsenic trioxide. The salts of arsenic may possibly be formed, but if so, they are immediately hydrolyzed by the water. More time is needed to complete some replacements than others. Arsenic also replaces silver from some non-aqueous solutions, although in still others it has no action.

Mercury.

Mercuric nitrate $Hg(NO_3)_2$—saturated solution in water. A white precipitate of mercurous nitrate was instantaneously formed on the addition of metallic arsenic. Twelve hours later, this white precipitate had entirely disappeared, leaving a heavy deposit of metallic mercury. The reaction was accompanied by an evolution of brown fumes of nitrogen dioxide. Microscopic examination of the evaporated solution showed the arsenic to be present as arsenic trioxide. The reaction can be expressed by an equation similar to the one expressing the reaction with silver nitrate:

$$3Hg(NO_3)_2 + 8As = 4As_2O_3 + 6NO + 3Hg$$

Mercurous sulfate (Hg_2SO_4) 100 g. per L. solution in water containing sulfuric acid. It was necessary to add sulfuric acid to the solution to prevent the formation of the insoluble basic salt. Several months were required to replace completely the mercury in solution by arsenic. The arsenic remained in solution which

contained an excess of acid as stated. The reaction is best expressed by this equation:

$$3Hg_2SO_4 + 2As + 3H_2O = 3H_2SO_4 + As_2O_3 + 6Hg$$

Mercurous cyanide $Hg(CN)_2$ 100 g. per L solution in water. The action of arsenic on this solution was very slow. After standing for 3 months, a white precipitate was formed which, upon standing for another 3 months, disappeared, and in its place a heavy deposit of metallic mercury was found. Even then, all of the mercury had not been replaced by arsenic. Upon evaporation to dryness, the odor of hydrocynanic acid was prevalent, and crystals of arsenic trioxide were found. This equation expresses the reaction:

$$3Hg\ (CN)_2 + 2As + 3H_2O = 6HCN + As_2O_3 + 3HG$$

Mercuric acetate $(CH_3COO)_2Hg$—25 g. per L. solution in water. In this experiment some peculiar growths formed on the piece of arsenic. Yellow tufts or trees were first observed. These later grew to be tall threads with knobs on the top. These tufts were most likely raised by dissolved air collecting in them. Within a week, these tufts were replaced by white needle-like crystals, and later by metallic mercury. The mercury was never entirely replaced from the solution. The reaction which took place may be expressed by this equation:

$$3(CH_3COO)_2Hg + 2As + 3H_2O = \\ 6CH_3COOH + As_2O_3 + 3Hg$$

Mercury bichloride $HgCl_2$—saturated solution in water. Mercurous chloride was slowly precipitated. When the solution had reached an equilibrium after standing several months, traces of both arsenic and mercury could be found in the solution. The reaction can be expressed by an equation showing replacement and hydrolysis:

$$3HgCl_2 + 2As + 3H_2O = 6HCl + As_2O_3 + 3Hg$$

A saturated solution of *mercuric bromide* behaved similarly, leaving a deposit of mercurous bromide. The equation expressing the reaction is similar to the one for mercury bichloride:

$$3HgBr_2 + 2As + 3H_2O = 6HBr + As_2O_3 + 3Hg$$

Mercurous nitrate ($HgNO_3$)—saturated solution in water. Mercury was immediately formed with the evolution of nitrogen dioxide, and the formation of arsenious acid. The reaction may be expressed thus:

$$3HgNO_3 + 4As = 2As_2O_3 + 3Hg + 3NO$$

Mercurous sulfate (Hg_2SO_4)—saturated solution in water. The actions of arsenic on this solution was slow, but arsenic completely replaced the mercury and formed arsenious acid. The equation expressing the reaction is of the same general type as those above:

$$3Hg_2SO_4 + 2As + 3H_2O = 6Hg + 3H_2SO_4 + As_2O_3$$

Mercuric palmitate—saturated solution in anhydrous ethyl alcohol. A white precipitate was formed which was probably mercurous palmitate. No arsenic could be detected in the solution.

Mercuric stearate—saturated solution in pyridine. A gray deposit of metallic mercury was formed within a few days, and also a brown gell-like growth on the bottom of the container.

From the above experiments it is evident that the primary action of arsenic on the mercuric salts is that of a reducing agent, forming the mercurous salts. In most cases the mercury is then replaced by the arsenic to form arsenic trioxide and metallic mercury.

Copper

Cupric chloride ($CuCl_2$) 100 g. per L. solution in water. The action of arsenic on this solution was very slow, and only a small amount of copper was displaced from the solution. Some cuprous chloride was also precipitated. The slight amount of arsenic which entered the solution was found as arsenious acid. The equation which best accounts for the products formed is:

$$4CuCl_2 + 2As + 3H_2O = 2Cu + 2CuCl + 6HCl + As_2O_3$$

Copper sulfate ($CuSO_4$) —100 g. per L. solution in water. The solution underwent no apparent change on long standing, but on evaporation to dryness, crystals of arsenic trioxide were found in goodly amount. This reaction could be hastened by passing an electric current through the solution. A piece of

arsenic was used as the positive electrode, and a piece of platinum as the negative. By the use of a single dry cell the copper was entirely replaced by the arsenic. Upon evaporation of this solution, particularly large and well formed crystals of arsenic trioxide were obtained. The reaction in either case can be expressed by this equation:

$$3CuSO_4 + 2As + 3H_2O = 3H_2SO_4 + 3Cu + As_2O_3$$

Copper nitrate $Cu(NO_3)_2$—100 g. per L. solution in water. The solution appeared to remain unchanged for six months, but upon evaporation, crystals of arsenic trioxide were found among the crystals of copper nitrate. The slight reaction that did take place can be expressed as in the case of the other nitrates:

$$3Cu\ (NO_3)_2 + 8As = 4As_2O_3 + 3Cu + 6NO$$

Copper acetate $(CH_3COO)_2\ Cu$—50 g. per L. solution in water. On long standing in contact with this solution, the arsenic seemed to corrode and crumble, and at the same time, a yellow coat of metallic copper was formed on it. The solution became colorless and the action was complete within a month. The arsenic had gone into solution as arsenious acid. This equation expresses the reaction:

$$3(CH_3COO)_2\ Cu + 2As + 3H_2O = \\ 6CH_3COOH + As_2O_3 + 3Cu$$

Copper tartrate $(CuC_4H_4O_6)$—saturated solution in water. The arsenic had entirely replaced the copper, after a month's standing, and had gone into solution as arsenious acid, leaving the solution colorless. The reaction is as follows:

$$3CuC_4H_4O_6 + 2As + 3H_2O = 3H_2C_4H_4O_6 + 3Cu + As_2O_3$$

Copper phosphate $Cu_3(PO_4)_2$—saturated solution in water. The action was similar to that of the tartrate solution thus:

$$Cu_3(PO_4)_2 + 2As + 3H_2O = 2H_3PO_4 + As_2O_3 + 3\ Cu$$

Copper arsenate and arsenite, $Cu_3\ (AsO_4)_2$ and $Cu_3(AsO_3)_2$, saturated solutions in water. These two salts acted similarly.

The action was the same as in the tartrate and phosphate solutions, namely copper was completely replaced. These reactions are expressed by the following equations:

$$Cu_3(AsO_4)_2 + 2As = 3Cu + As_2O_3 + As_2O_5$$
$$Cu_3\ (AsO_3)_2 + 2As = 3Cu + 2As_2O_3$$

Copper abietate and oleate—50 g. per L. solutions in xylol, also in toluol. The metallic arsenic caused a heavy flocculent precipitate to form in both cases, but no arsenic could be found in solution. The precipitate was slimy and sticky so that it could not readily be separated from the solution and inspected further.

Copper stearate and palmitate saturated solutions in chloroform, also in anhydrous ether. A slight coating of metallic copper was formed on the arsenic within a week.

Copper glycine $(CH_2NH_2COO)_2Cu$—saturated solution in water. No copper remained in solution after standing a week in contact with the arsenic. That is, all copper was deposited in the metallic state.

Copper oleate, molten. Metallic arsenic was allowed to stand for one month in molten copper oleate. The mixture was kept at a constant temperature of 120° to 130° C. In order to have a check on the effect of heat alone upon copper oleate, a control of copper oleate alone was kept under the same conditions. At the end of the month, both the mixture and the control had precipitates of metallic copper on the bottom of the containers. The amount of copper deposited in the mixture was far greater, however, than the amount in the control. Upon cooling, the control was still green and solid, whereas in the parallel experiment containing the arsenic a heavy, mobile, brown oil was formed. The unchanged copper oleate could be filtered from this oil. After filtration, the brown oil was much less viscous. A light yellow oil could be distilled from this brown oil at 250° C., under reduced pressure. No arsenic could be detected either in the light oil, or in the heavier brown oil. The action of the arsenic seems to have been entirely catalytic in this case.

The experiments on the copper salts show that copper is re-

placed from the aqueous solutions of the common copper salts by metallic arsenic. In the non-aqueous solutions this is not always the case.

Antimony and Bismuth.

A series of experiments was undertaken as follows: Acetone solutions of the chlorides of arsenic, antimony and bismuth were prepared. Into separate solutions of arsenic chloride, 3 g. of antimony and bismuth were placed respectively. The antimony chloride solution was treated similarly with arsenic and bismuth, and the bismuth chloride with arsenic and antimony. After standing for several months, no trace of replacement could be detected in any case by careful qualitative analysis.

Other Metals.

Platinic chloride ($PtCl_4$)—10 g. per L. solution in water. The platinum was slowly replaced by arsenic, leaving a solution of arsenious acid. The reaction may be expressed thus:

$$3PtCl_4 + 4As + 6H_2O = 3Pt + 2As_2O_3 + 12HCl$$

Gold chloride ($AuCl_3$)—100 g. per L. solution in water. The gold was first thrown out of solution as a fine yellow precipitate, but a heavy deposit of metallic gold was soon formed. The arsenic crystallized from the solution as arsenic trioxide upon evaporation. This reaction can be expressed as follows:

$$2AuCl_3 + 2As + 3H_2O = 2Au + As_2O_3 + 6HCl$$

Ferric chloride ($FeCl_3$)—250 g. per L. solution in water. Ferric chloride was reduced to the ferrous condtion by the metallic arsenic. This equation shows how the reduction takes place:

$$6FeCl_3 + 2As + 3H_2O = 6FeCl_2 + As_2O_3 + 6HCl$$

Cadmium sulfate ($CdSO_4$)—250 g. per L. solution in water. Arsenic reduced cadmium sulfate to the yellow sulfide, and went into solution as arsenious acid. The reduction took place as follows:

$$3CdSO_4 + 8As = 3CdS + 4As_2O_3$$

White precipitates were formed on the addition of arsenic to concentrated solutions of *zinc chloride, aluminum sulfate, and lead nitrate.*

Arsenic had no effect on concentrated solutions of the sulfates of nickel, cobalt, or manganese.

The ability of some of the common metals to replace arsenic from pure anhydrous arsenic trichloride is shown in the Table IX. The data indicate the action observed at room temperature on standing, and also upon heating to 100° C.

TABLE IX.

Action of Metals on Anhydrous Arsenic Trichloride.

Metals	Room temperature	100° C.
Sodium	Immediate plating	Violent reaction (burned)
Magnesium	Immediate plating	Violent reaction
Aluminum	Immediate plating	Strong reaction
Zinc	Immediate plating	Strong reaction
Cadmium	Slight plating after standing	Slight reaction
Iron	Slight plating after standing	Slight reaction
Cobalt	Slight plating after standing	Slight reaction
Nickel	Slight plating after standing	Slight reaction
Lead	Immediate plating	Strong reaction
Tin	Immediate plating	Strong reaction
Bismuth	Slight tarnish after standing	Slight reaction
Antimony	Slight tarnish after standing	Slight reaction
Copper	Good plating after standing	Strong reaction
Mercury	Slight black deposit after standing	No further reaction
Silver	No plating	No reaction
Platinum	No plating	No reaction
Gold	No plating	No reaction
Molybdenum	No plating	No reaction

From the replacement reactions above described in detail, and especially from the data in Table IX, one would conclude that arsenic certainly lies higher in the series than silver, platinum and gold. Such a conclusion would be in line with the results of the single potential measurements given in the first part of this paper.

Referring to Table IX, it will be noted that bismuth, antimony and mercury were tarnished when introduced into pure $AsCl_3$. With the help of G. G. Pierson, a graduate student in this labora-

tory, this matter was followed out somewhat further, and it was found that by conducting the experiment much longer (30 days), bismuth, antimony, mercury, and even silver will noticeably replace arsenic. The action goes on much better in $AsBr_3$, which was heated so as to keep it in a molten state. Mercury reacts particularly rapidly upon $AsBr_3$. Neither iron, cobalt, nickel, chromium, or molybdenum will replace arsenic to a notable extent in any case. On the other hand, antimony, bismuth and tin, when heated with $AsBr_3$, replace arsenic completely, forming metallic arsenic and the bromides of the other metals. In $AsBr_3$ even silicon and selenium have been found to replace arsenic. These reactions and many others have been studied in this laboratory by Prof. Kahlenberg and Mr. Pierson, and the results obtained will be published soon.

It is clear, however, that as far as replacement reactions are concerned, one can say that arsenic is not replaced by gold, platinum, palladium, and molybdenum, and that chromium, iron, cobalt and nickel, are also unable to replace arsenic. These facts would indicate that from a knowledge of the single potential of arsenic, one cannot with certainty predict as to what metals it will replace, or what metals will in turn replace it.

Torbern Bergman, in the latter part of the 18th century, was the first one to arrange the metals in the order in which they will replace another in solutions. Since that time the single potentials of the various metals toward different electrolytes have been measured, and it has been found that the potential series, in general, runs parallel with the replacement series. It is clear, however, from the present research that after all one cannot with certainty predict what replacements will take place from a knowledge of electrical potentials. All that one can say is that *the replacing power of a metal is a highly specific property of that metal, and also of the liquid in which it is immersed in the actual experiment.* The matter really merits further detailed study in regard to all of the individual metals; for the facts now at hand seem to indicate that there is merely a parallelism between the replacement series of the metals and the single potential series, and not a relation of cause and effect.

DISCUSSION.

WM. BLUM[1]: Before we can consider the usefulness of the electrochemical series, it is necessary to define it. In order to have the metals in corresponding environments, their normal potentials are usually defined in terms of hypothetical solutions, which contain normal concentrations of the metal ions, or in which the ions have equivalent "activities". The variation in the order of the metals in different published tables is due to the difficulties of computing the ion concentrations or activities from existing data, and not to essential differences in the definitions.

As above defined, the normal potentials of the metals indicate merely their ability to replace each other in solutions of normal or at least corresponding metal ion concentrations. The discrepancies noted in the behavior of arsenic are not dissimilar to other apparent contradictions that have been explained or even predicted from the normal potentials; such as the fact that tin and lead mutually replace each other from perchlorate or fluoborate solutions; or that copper precipitates zinc from certain cyanide solutions.

It is probable that a study of the potential relations in the solutions used would indicate that the potential is in each case a measure of the tendency of the metal to pass into or out of solution. Whether such potentials can be expressed in terms of ion concentration will depend upon our knowledge of such ion concentrations or activities in the specific solutions used. For many non-aqueous solutions or fused salts, such information is not now available, and hence the electrochemical series cannot be directly applied to them.

LOUIS KAHLENBERG: Some of these reactions go on in insulating solutions. How are you going to determine the number of ions there by the potential method? The soaps of the heavy metals do not conduct in chloroform or benzol. It is tantalizing that they should act without ions being present, but they do so.

COLIN G. FINK[2]: I should like to ask Dr. Kahlenberg whether he has found any explanation for the phenomenon recorded on

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page 508; "Silver cyanide—only after standing for one month, was a sufficient amount of silver deposited to form a thin coating of white metallic silver, which adhered tightly to the arsenic. Although the solution still contained quantities of silver, no more could be displaced, when more arsenic was added and the mixture allowed to stand 6 months." Why do you get silver at first?

Referring to page 502, line 8: "It should perhaps be added here that in all cases in Tables IV and V beautiful, blue black deposits of arsenic were obtained, and, indeed, microscopic examination of each arsenic plated electrode revealed no flaws in the coating."

It is hard to understand why you get such low voltages for arsenic on cobalt. As compared to arsenic mechanically attached or glued to platinum, you get a voltage of 0.544, unless perhaps the coating on cobalt is not arsenic but an alloy or compound.

Louis Kahlenberg: We have not followed out the potassium silver cyanide experiment further. The thickness of the blue black deposits of arsenic has not been measured.

As to the single potential of arsenic, it has been definitely determined to be about 0.55 v. which enables one to assign to arsenic a definite place if voltages are the basis of the arrangement of the series. On the other hand, the replacement experiments clearly show that, according to the nature of the solution used, arsenic may lie above copper or way below silver, so that one cannot use the electrode potential to foretell the replacing power.

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